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QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS

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AUTHORIZED TRANSLATION

THIRD ENGLISH FROM THE REVISED AND GREATLY ENLARGED FOURTH GERMAN EDITION

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FIRST THOUSAND

NEW YORK

JOHN WILEY & SONS

LONDON: CHAPMAN & HALL, LIMITED

1898

3 713 242

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PREFACE TO FOURTH EDITION.

The present edition, revised with the assistance of Dr. Löb, differs from the previous editions in that the Introduction has been augmented by the insertion of a section devoted to theory. This was made the more necessary, since the investigations of recent years have been chiefly devoted to the explanation of the reactions in solutions, and the determination of the electrical magnitudes. The necessity of specific directions concerning electrode tension, current strength and decomposition tension has been demonstrated. The author, with the co-operation of his assistants, has experimentally determined these electrical magnitudes, not only for his own methods for the determination and separation of the metals, but also for a number of other methods, and has incorporated them in the text. Additional methods by other authors, in which directions concerning these important factors are wanting, have been omitted, in consideration of the fact that these are either uncertain or entirely impractical; mention of them has, however, been made in the references to the literature.

The book has been made more complete by the description of various measuring instruments, sources of current and apparatus; together with an explanation of simple and complete appliances for carrying out electrolytic experiments. These have been illustrated by a large number of new cuts, in the text and in the appended tables.

The publishers have spared neither pains nor expense to make these new illustrations as perfect as possible; I feel called upon to express here my full appreciation of this fact.

A. Classen.

Aachen, January 18, 1897.

TRANSLATORS' PREFACE.

The Author's Preface to the Fourth Edition points out so fully the improvements over preceding editions, that the translators need add nothing. It is plainly a more complete, scientific and logically arranged work than heretofore.

The translators have made some additions, as had their senior in previous editions; and have corrected some errors in the German edition, apparently the result of hasty compilation. The "Special Part" of former German editions (which is omitted in the fourth) has been retained in the form of an appendix, and has been revised and brought up to date. In addition to this a carefully prepared index has been added, and the translators believe that the value and convenience of the work is thereby much enhanced.

William Hale Herrick,
Bertram B. Boltwood.

January, 1898.

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PART I.—GENERAL PART.

INTRODUCTION.*

Water acidified with sulphuric acid is decomposed into its elements, hydrogen and oxygen, when a galvanic current is passed through it; a large number of compound substances conduct themselves in a similar manner. This galvanic decomposition is called electrolysis, and the substances which are decomposed by the electric current are known as electrolytes. The substances into which electrolytes are separated by the electric current are naturally divided into two groups: Those which separate at the positive electrode, or anode (connected with the + pole of the source of the current), and which are therefore the electro-negative constituents, are called anions; those which separate at the negative electrode, or cathode (connected with the — pole of the source of the current), the electro-positive constituents, are called cathions.

The metalloids, or electro-negative acid groups, therefore appear at the positive electrode, while the metals are separated at the negative electrode.

* An elementary knowledge of galvanic action is assumed.

For instance, if the electric current is passed through the solution of a haloid salt, the halogen is separated at the anode, the metal at the cathode.

$$CuCl_2 = Cl_2 + Cu,$$
$$ZnCl_2 = Cl_2 + Zn.$$

Oxygen salts act in a similar manner.

$$CuSO_4 = SO_4 + Cu,$$
$$Cu(NO_3)_2 = (NO_3)_2 + Cu.$$

Many acids are decomposed in a similar manner.*

$$H_2SO_4 = SO_4 + H_2,$$
$$2HCl = Cl_2 + H_2.$$

The substances formed by electrolytic decomposition, however, generally undergo further chemical change, or are acted on by the electrodes; various *secondary reactions* take place.

In the electrolysis of a solution of copper sulphate between platinum electrodes, the secondary process consists in the reaction with water of the group SO_4, which cannot exist uncombined.

$$SO_4 + H_2O = H_2SO_4 + O.$$

The evolution of oxygen gas, which is partially due to this secondary reaction, is observed at the positive pole. Primarily the water itself splits off oxygen in the electrolysis of aqueous solutions.

* Some acids are not decomposed by the electric current; e.g., silicic, carbonic, and boric acids.

In the electrolysis of hydrochloric acid, the chlorine set free at the anode reacts with water, forming hypochlorous acid, chloric acid, perchloric acid, etc. Similar secondary reactions are observed in the electrolysis of chlorides. If a solution of ammonium chloride, for example, is submitted to electrolysis the nascent chlorine acts on the undecomposed salt, with the production, among other substances, of nitrogen, or nitrogen chloride. Haloid salts of the alkaline earths show similar phenomena.

Nitric acid, on electrolysis, gives in the first place

$$8HNO_3 = 4H_2 \text{ (cathion)} + 8NO_3 \text{ (anion)}.$$

The latter then splits up further:

$$4N_2O_6 = 4N_2O_5 + 2O_2 \text{ (anion)}.$$

The oxygen is given off, while the anhydride forms nitric acid again with water:

$$4N_2O_5 + 4H_2O = 8HNO_3.$$

The hydrogen, on the contrary, which appears as cathion, is not set free but acts reducingly on the nitric acid present:

$$4H_2 + HNO_3 = NH_3 + 3H_2O.$$

In the presence of sulphuric acid, or a sulphate, this decomposition is complete, the final product being ammonium sulphate.

This decomposition of nitric acid is of practical importance in chemical analysis. From a nitric acid solution which contains copper and zinc, the former metal only is reduced; this fact can be utilized for the separation of the two metals. If,

now, the current is allowed to pass for a long time after the reduction of the copper, the nitric acid is gradually converted into ammonia, and the zinc then separates from the solution.

If the salts of metals which decompose water at ordinary temperatures (alkalies and alkaline earths) are electrolyzed, secondary reactions occur at the negative electrode:

$$\begin{aligned} K_2SO_4 &= SO_4 \text{ (anode)}, \\ &\quad K_2 \text{ (cathode)}, \\ (SO_4 + H_2O &= H_2SO_4 + O), \\ K_2 + 2H_2O &= 2KOH + H_2. \end{aligned}$$

The decomposition products, then, are sulphuric acid and oxygen at one electrode, potassium hydroxide and hydrogen at the other. It must be borne in mind, however, that a small portion of the hydrogen and oxygen formed owes its existence to the primary electrolysis of the water.

The metals disengaged at the negative electrode may yield secondary products by acting on the substances in solution. So, for instance, in the electrolysis of cupric chloride, the separated copper reacts with the cupric chloride to form cuprous chloride; copper acetate yields, at the cathode, a mixture of copper and cupric (or cuprous) oxide.

In the electrolysis of organic compounds, the groups set free at an electrode may be decomposed in a manner analogous to that noted in inorganic compounds, and yield various products.

The electrolysis of potassium acetate should yield, as final products, potassium (potassium hydroxide) and acetic acid.

Instead of this, the acetic acid splits either into carbon dioxide and ethane, or ethylene is formed by the action of oxygen on the ethane.

Potassium valerate yields, in addition to valeric acid,

carbon dioxide and octane; the latter is oxidized by continued electrolysis to isobutylene and water.

Sodium succinate yields, among other products, ethylene and carbon dioxide; potassium lactate breaks up into carbon dioxide and acetaldehyde.

For the purposes of quantitative chemical analysis, only such solutions are adapted, as indicated by the foregoing, as are decomposed completely by the current without the formation of injurious intermediate products. Solutions which contain a free inorganic acid are well adapted to electrolysis, because of their high conductivity.

Of all compounds of the metals, the *double oxalates* are the best adapted to quantitative analysis.* Oxalic acid is decomposed by the electric current:

$$C_2H_2O_4 = 2CO_2 \text{ (anode)},$$
$$H_2 \text{ (cathode)}.$$

When potassium oxalate is subjected to electrolysis, the principal decomposition-products are:

$$K_2C_2O_4 = 2CO_2 \text{ (anode)},$$
$$K_2 \text{ (cathode)},$$
$$K_2 + 2H_2O = 2KOH + H_2 \text{ (cathode)},$$
$$2KHO + 2CO_2 = 2KHCO_3.$$

When ammonium oxalate is used, the decomposed solution contains hydrogen ammonium carbonate. The latter partly decomposes into ammonia and carbon dioxide.

In the electrolysis of double oxalates, e.g., of zinc ammo-

* Classen, Ber. d. ch. Ges., **14**, 1622, 2771; **17**, 2467; **18**, 1104, 1687; **19**, 323; **20**, 504; **21**, 2900.

nium oxalate, decomposition takes place as follows: Zinc oxalate breaks up into zinc and carbon dioxide, and ammonium oxalate into ammonium and carbon dioxide. The carbon dioxide, which separates at the positive pole, combines with the ammonium to form hydrogen ammonium carbonate, as above explained.

In the decomposition of oxalates there are no unfavorable secondary reactions. All oxalates are decomposed by the electric current with greater or less ease, and the reduced metals are not attacked by the decomposition-products, even when the current becomes weaker during the reaction. When the reaction is complete, the solution can be poured off at once, and the weight of the separated metal determined. (See further details later.)

THE ION THEORY.

Before proceeding to a description of the appliances and methods of quantitative analysis, the reactions which take place in solutions during their decomposition, together with the magnitudes which here come into consideration, should be made perfectly clear.

The ion theory, proposed in connection with the researches of van't Hoff, by the Swedish investigator Arrhenius, furnishes us with a comprehensive picture of the same. According to this theory, a partial splitting up of the dissolved compounds into their component parts takes place in aqueous solutions; a dissociation which, in contradistinction to the ordinary, is called *electrolytic dissociation*.

In the case of a sodium chloride solution, for example, many phenomena, such as the osmotic pressure, the lowering of the freezing-point, and others, necessitate the assumption that, besides the particles of undecomposed NaCl, separate

particles of Na and Cl are present in the solution. The latter are entirely different from atomic Na and Cl, since it is of course impossible to conceive of a Na atom, which reacts violently with water, as existing free in an aqueous solution.

The *difference* between these electrolytic dissociation products and atoms *lies in an unlike content of energy*. This of course materially affects the other properties.

While the atom in itself must be considered non-electric (containing as much positive as negative electricity), it is necessary to attribute a certain electric charge to the products of electrolytic dissociation. These electrically charged particles are called *ions* (*ἰόντες*, the wandering), a name given to them by Faraday.

The phenomena of the osmotic pressure and the depression of the freezing-point, already mentioned, have identified with electrolytic dissociation, and accordingly with ions, certain classes of chemical compounds, namely, acids, bases, and salts, but not indifferent organic compounds. Since it has been shown that the former compounds, and indeed only these and no others, conduct the electric current in aqueous solutions, the existence of ions and the characteristic of being decomposed by the electric current have been brought into causal relation.

The substances which are electrolytically dissociated in solution, and therefore conduct the electric current, are called electrolytes; those which are not dissociated into ions and do not permit the passage of the current, non-electrolytes. Acids, bases, and salts are accordingly electrolytes; all other substances, such as chloroform, benzene, ether, sugar, etc., non-electrolytes.

Relative to the formation of ions, all acids exhibit a common characteristic in yielding hydrogen ions; correspondingly all bases give hydroxyl ions.

An acid is accordingly dissociated as follows:

HCl	into	H	Cl
H_2SO_4	into	H_2	SO_4
HNO_3	into	H	NO_3
$C_2O_4H_2$	into	H_2	C_2O_4
CH_3COOH	into	H	CH_3COO, etc.

By the electrolytic dissociation of acids, therefore, all of those hydrogen atoms, which are replaceable by metals on neutralization with bases, are brought into the state of ions; at the same time the corresponding acid radicals pass over into the ionic condition.

The dissociation of bases is analogous:

$NaOH$	into	Na	OH
NH_4OH	into	NH_4	OH
$Ca(OH)_2$	into	Ca	$(OH)_2$, etc.

All the hydroxyl groups, which are replaceable by acid radicals on neutralization with acids, change to the ion condition; and simultaneously the basic radicals, i.e., the metals.

Salts are accordingly dissociated into metal and acid ions.

When the current passes, a part of the ions migrate to the positive electrode, a part to the negative electrode. Since the ions possess an electric charge, those attracted by the positively charged electrode must be negatively charged (*anions*), and those attracted by the negative electrode positively charged (*cathions*).

Hydrogen and all metals are electro-positive; halogens and acid radicals, electro-negative. The former are cathions, the latter anions. Therefore when a salt of a metal is electrolyzed, the metal separates at the negative electrode, the acid radical at the positive electrode.

It has been demonstrated that the electrolytic dissociation increases with the dilution, and proportionally to it the electrical conductivity of the ions also. Arrhenius therefore drew the conclusion that the ions alone conduct the current, and that the undissociated portion takes no part in the electrolysis. This assumption has been proved correct, and through it electrolytic dissociation presents an entirely different aspect.

The primary products which are set free at the electrodes are not separated by the current, but existed previously in the solution in the form of cathions and anions.

Since the substances separate at the electrodes in an atomic, non-electric condition, while the ions possess an electric charge, a discharge of the ions must take place at the electrodes. Such is in fact the case. The negatively charged electrode attracts the positively charged cathions, and on their coming into contact a neutralization of equivalent parts of positive and negative electricities takes place, accompanied by the disappearance of electricity. The separation of the substance in an atomic form is then possible. The work done by the electric current consists in the attraction and discharge of the ions, but *not* in the decomposition of the dissolved compound.

What has been said of the cathion naturally applies in a similar manner to the anion.

The degree of dissociation at a certain concentration [and temperature] is a fixed magnitude for every substance. Here the objection might be raised, for example, that in a copper sulphate solution in which $\frac{1}{3}$ of the copper sulphate is split up into Cu and SO_4 ions and $\frac{2}{3}$ is present as undissociated salt, the electrolysis must come to a standstill after the third of the copper has been removed, since there are no more copper ions present. Experiment shows that all the copper may be separated. This phenomenon is explained by the law of mass action, according to which the product of the ion con-

centrations remains constant at a fixed concentration of the solution. In other words, if copper ions disappear from the solution owing to the removal of the metal, the undissociated salt present dissociates and furnishes new copper ions. This process continues until all the copper ions have been removed by precipitation as atoms. What is true of copper sulphate is true of all acids, bases, and salts, and anions behave similarly to cathions.

FARADAY'S LAW.

This law, which is named from its discoverer and is the basis of all electrolytic phenomena, includes the two following propositions:

1. The quantities of ions separated at the electrodes during equal intervals of time are directly proportional to the current strength.

2. Equal quantities of electricity separate the ions in proportion to their chemical equivalent weights.

The truth of the first statement may be readily demonstrated by electrolyzing a copper sulphate solution for ten minutes with a current of certain strength and determining the weight of the separated copper. If now in a second operation a current of twice the former strength be passed through the same solution for an equal length of time, the weight of the copper separated in the second case will be twice as great as that precipitated in the first experiment.

The second proposition, called in brief Faraday's Law, is proved experimentally by passing the same current simultaneously through a series of solutions of metallic salts and weighing the quantities of metals which separate. It will then be found that the weights are proportional to the chemical equivalent weights of the metals. Accordingly solutions of silver nitrate, cupric chloride, and ferric chloride when decom-

posed by the same current, yield precipitates of metals, the weights of which bear the following ratio to one another:

$$108 : \frac{63}{2} : \frac{55.9}{3}.$$

The ratio when silver nitrate, cuprous chloride, and ferrous chloride are used is correspondingly,

$$108 : 63 : \frac{55.9}{2},$$

so that the equivalent weight is dependent upon the valence of the metal in the compound employed. That which may be conveniently carried out in the case of the metals, i.e., the cathions, holds true similarly in the case of the anions.

The law of Faraday, regarded in the light of the ion theory, leads to a series of new conclusions. It declares that equal currents of electricity always separate equal quantities of univalent, half the quantities of bivalent, and one-third the quantities of trivalent ions. This separation consists in the discharge of the electrically charged ions; therefore it follows that equal quantities of univalent ions are the carriers of equal electric charges, that the same quantities of bivalent ions bear twice, of trivalent ions three times, as great charges.

Consequently all univalent ions, independent of their chemical nature, bear equal quantities of electricity, all bivalent ions twice the quantity, etc. The magnitude of this charge is considerable. Experiment has shown that by the action of 96,500 coulombs of electricity on an electrolyte, a quantity of ions equal in grams to their atomic weight divided by their valence always passes over into the atomic condition, or, as it may be stated, by 96,500 coulombs a gram equivalent of ions will be discharged, or, better, neutralized on the electrode. For this neutralization the ions must carry a

quantity of electricity equal, but opposite in sign, to that supplied by the source of current to the electrodes. A gram equivalent of ions must therefore be the bearer of 96,500 coulombs.* This conclusion, arrived at by v. Helmholtz, leads to the assumption that every bond of valence of an elementary or complex ion is charged with the same quantity of positive or negative electricity, which, similarly to an electric atom, cannot be further divided.

OHM'S LAW.

Ohm's Law holds good for solutions as it does for metals:

$$C = \frac{E}{R}, \quad E = C \cdot R.$$

When suitable units are chosen, the current strength is equal to the quotient of the electromotive force divided by the resistance.

The *ampere* serves as the unit of current strength, and is that current strength by which, in one second, 0.328 mg. of copper will be precipitated.† The unit of resistance is the resistance (at 0°) of a column of mercury having a length of 106.3 cm. and a cross-section of 1 sq. mm. It is called the *ohm*. The unit of electromotive force is the *volt*, and is defined by the equation

$$1 \text{ ampere} \times 1 \text{ ohm} = 1 \text{ volt},$$

$$\text{ampere} = \frac{\text{volt}}{\text{ohm}}.$$

---

* "The quantity of electricity necessary for the separation of a gram equivalent, i.e., 96,540 coulombs, is to be denoted by the symbol F, in remembrance of Faraday." Report of Commission on Electrical Units, Deutsche Elektrochemische Gesellschaft. Zeit. f. Elektrochemie, 1897-98, p. 36.—*Trans.*

† An ampere may be also defined as the strength of the current which flows through a resistance of 1 ohm when the electromotive force is equal to 1 volt.—*Trans.*

An electromotive force of one volt with a resistance of one ohm gives a current strength of one ampere.

Every source of current furnishes a certain electromotive force; it possesses a certain tension. If the two poles of a source of current are connected by a conductor, there takes place along this connection a fall of potential which is proportional to its resistance. If an electrolyte, into which extend two electrodes, is included in the circuit, there arises a difference of potential between the electrodes which is called the *electrode tension*. This tension at the electrodes is of considerable importance in electrolysis, since it denotes that electromotive force which comes into action in the cell itself. Each of the three factors given in Ohm's Law is of significance for quantitative electrolysis; we will next proceed to their consideration.

TENSION AND ITS SIGNIFICANCE FOR ELECTROLYSIS.

As quantitative electrolysis is employed chiefly for the determination of metals, it will be well to here consider some of the general properties of solutions of metallic salts.

In accordance with present theory, the origin of an electromotive force is explained as follows: If a strip of metal, zinc for example, be dipped into an electrolyte, say zinc chloride, the zinc ions present in the solution will have a tendency to discharge their electricity upon the zinc and to pass over into an atomic condition. This tendency may be considered as a pressure directed from the liquid toward the metal, and is known as the *osmotic pressure of the ions*. The metallic zinc, however, exerts a pressure in the opposite direction, which is due to the tendency of the zinc atoms to pass into the solution and assume the condition of ions, and is opposed to the separation of the ions already present, which strive to leave the

electrolyte as atoms. This latter pressure is known as the *electrolytic solution pressure.*

Since the ions are bearers of electric charges, it is evident that the simultaneous action of these two pressure-forces is intimately connected with the production of electricity, and experience has taught that the electromotive force between the liquid and the metal may be considered a function of these two pressures.

Osmotic pressure of the ions and electrolytic solution pressure cause currents in opposite directions. The positively charged ions of the salt solution tend, as a result of the osmotic pressure, to give up their charges to the exposed metal and to charge this positive; while, on the other hand, the electrolytic solution pressure forces positive ions out from the metal and into the solution, leaving an equivalent negative charge upon the metal itself.

If a similar course of reasoning be applied to the case where an electric current is passed between two platinum electrodes which dip into a solution of a metallic salt, the following conditions will be recognized. A definite difference of potential will exist between the electrodes, as a result of which metal will be separated on the negative pole, and, in general, oxygen on the positive pole. As soon, however, as the metal and oxygen have passed over into the atomic condition, the electrolytic solution pressure of each comes into action and operates to drive them back into the form of ions. An electromotive force opposed to that of the primary current is thereby set up. This electromotive force, which may under certain conditions have a tension higher than that of the primary current, is the cause of a current called the *polarization current.* Polarization must always appear when unattacked electrodes, as those of platinum, which are exclusively used in quantitative electrolysis, are employed.

The tension required for electrolysis may always be determined from the consideration of the above conditions. It must in all cases be greater than the resulting polarization current, for otherwise, at the commencement of decomposition, the electromotive force of the primary current would be counterbalanced by the polarization tension and electrolysis would be entirely prevented.

Le Blanc, who made a careful study of the values of the tensions required for the decomposition of various solutions, directed attention to the fact that for the continued electrolysis of any solution a definite minimum tension, dependent directly upon the polarization phenomena, is required.

This so-called *decomposition tension value* is often given as a measure in quantitative electrolysis, and by it is denoted that electromotive force at which the current is just able to pass through the cell. If the electromotive force of the primary current be denoted by E, the current strength by C, the resistance by R, and the polarization tension by P, then

$$E = C \cdot R + P.$$

E must satisfy this equation without C being equal to 0; then only can the current continuously decompose the solution.

Le Blanc determined the following values for the decomposition tension of $\frac{N}{1}$ solutions:

$ZnSO_4$	2.35 volts.	$Cd(NO_3)_2$	1.98 volts.
$ZnBr_2$	1.80 "	$CdSO_4$	2.03 "
$NiSO_4$	2.09 "	$CdCl_2$	1.88 "
$NiCl_2$	1.85 "	$CoSO_4$	1.92 "
$Pb(NO_3)_2$	1.52 "	$CoCl_2$	1.78 "
$AgNO_3$	0.70 "		

ACIDS.

Sulphuric acid	1.67 volts.	Pyroracemic acid	1.57 volts.
Nitric acid	1.69 "	Trichloracetic acid	1.51 "
Phosphoric acid	1.70 "	Hydrochloric acid	1.31 "
Monochloracetic acid	1.72 "	Hydrazoic acid	1.29 "
Dichloracetic acid	1.66 "	Oxalic acid	0.95 "
Malonic acid	1.69 "	Hydrobromic acid	0.94 "
Perchloric acid	1.65 "	Hydriodic acid	0.52 "
Dextrotartaric acid	1.62 "		

BASES.

Sodium hydroxide	1.69 volts.	$\frac{N}{4}$ Methylamine	1.75 volts.
Potassium hydroxide	1.67 "	$\frac{N}{2}$ Diethylamine	1.68 "
Ammonium hydroxide	1.74 "	$\frac{N}{8}$ Tetramethyl ammonium hydroxide	1.74 "

The sulphates and nitrates of the alkalies and alkaline earths have all nearly the same decomposition tension value, namely, about 2.20 volts.

The values of the decomposition tension for solutions of metallic salts are of decided importance for quantitative electrolysis, since by them is given the minimum tension required for the precipitation of a metal, and also the conditions under which several metals may be quantitatively precipitated from the same solution by simply altering the tension of the current. For example, zinc is not precipitated from a $\frac{N}{1}$ $ZnSO_4$ solution by a current having a tension of less than 2.35 volts, while a $\frac{N}{1}$ silver nitrate solution is decomposed at 0.70 volts. The silver may therefore be separated at a tension of less than 2.35 volts, the zinc remaining meanwhile in solution. After the separation of the silver, the electromotive

force may be increased to over 2.35 volts and the zinc precipitated as metal.

Kiliani, whose early death is to be greatly lamented, was the first to point out the importance of the tension for electrolytic separations. Somewhat later, Freudenberg, basing his work on Le Blanc's studies, carried out, in Ostwald's laboratory, a careful investigation of the exact relations. The results which he obtained will be given in the Special Part, in connection with the discussion of the determination and separation of the respective metals.

SIGNIFICANCE OF CURRENT STRENGTH.

Although the choice of tension makes the electrolytic separation of a metal possible, the condition of the resulting precipitate is first of all dependent upon the strength of the current which flows through the cell.

This follows from Faraday's law, since the number of ions which, by discharging on the electrodes, separate in the atomic condition, in the unit time, depends solely on the current strength.

Irrespective of the tension employed, a current of double strength will precipitate twice the quantity of metal in the same time. The current strength therefore determines the number of ions which will discharge within a given time, and correspondingly the rate of deposit on the electrode. With relation to the latter, however, a second factor, namely, the size and shape of the electrodes, is of decided importance, since the manner in which the metal is deposited by a certain current strength depends entirely on this. If the area of the electrode surface is small and the current density great, the individual atoms of metal are deposited one upon the other in such rapid succession that the precipitate does not adhere firmly to the electrode, but scales off. In quantitative elec-

trolysis, the firm adherence of the precipitate to the electrode is most essential for the determination of the weight of the separated material.

When, on the other hand, a very large surface is offered for the deposition, and a current of low current strength is employed, it is impossible for a compact layer to form and the metal will coat the surface in isolated patches. These conditions of precipitation are also useless for quantitative determinations.

The real significance of the current strength lies in its ratio to the area of the electrode surfaces. This is known as the *current density*, and as unit, a current strength of one ampere for 100 square centimeters electrode surface, has been chosen.

In this book, therefore, the current density will always be given with reference to 100 square centimeters of electrode surface, and will be expressed by the symbol ND_{100}.

If, for example, a current of 3 amperes flows through a cell, the electrode surface of which is equal to 250 sq.cm., an equal distribution of the lines of the electric current being assumed, the current of 3 amperes will be distributed over the 250 sq.cm., and therefore every 100 sq.cm. receives a current of $\frac{3}{2.5}$ ampere. The current density, therefore, $ND_{100} = 1.2$ ampere.

Although the current strength is the same at every point in the circuit, the current density of the cathode and anode have the same value only when the two electrodes have exactly equal dimensions.

In the determination of metals it is usually sufficient to know the current density at the cathode alone. On the other hand, to determine the halogens, for example, a knowledge of the current density at the anode is required.

The current strength, in the form of the current density, accordingly occupies an important place in quantitative electrolysis.

SIGNIFICANCE OF THE RESISTANCE.

The third factor in Ohm's Law, the resistance, is to be considered chiefly in the selection of the solvent which will be most suitable for the experiment, and the proper substances to be added to the electrolyte.

It is evident that with a certain given tension, which in every electrolysis may vary within certain limits, the speed of the operation depends upon the resistance of the solution, since by this the current strength is determined according to the equation

$$C = \frac{E}{R}.$$

It is therefore necessary to have the conductivity of the solution as high as possible. Since aqueous solutions are exclusively employed in quantitative electrolysis, this is accomplished by the addition of certain substances, the natures of which are dependent upon the chemical properties of the metals in the solution. In some cases acids are used; in others, bases or salts. The proper substances can only be determined by experience.

A fundamental requirement of the substance added and one which is independent of the chemical properties of the metal to be precipitated may, however, be stated. It must be a good conductor of the current and must form no decomposition products which are insoluble or are detrimental to the analysis. Alkalies and acids, which after their decomposition are again regenerated at the electrodes, are therefore suitable,

as are also organic acids, the decomposition products of which are given off in a gaseous form. This last condition is fulfilled by oxalic acid, which, on account of its great solubility, is of special importance in the electrolysis of metals, particularly in the form of double salts.

[A few words on the theory of the conductivity of solutions will perhaps be in place here. Since the passage of electricity through an electrolyte is always accompanied by the transference of material, the power which a solution has for conducting the electric current must depend directly upon the nature of the substances which are held in solution. As has already been stated, the ions alone are bearers of electric charges, the undissociated molecules taking no part in the transportation of electricity. The conductivity of a solution therefore depends upon the number of ions which it contains, and upon the nature of the ions themselves. If, in two equal volumes of a solution of the same substance, one contains twice as many ions as the other, the other physical conditions of both being the same, the conductivity of the former will be twice that of the latter.

The ratio of the dissociated part to the total amount of substance present is called the degree of dissociation. The degree of dissociation varies for different substances, but in all cases for fairly concentrated solutions increases with dilution. For very concentrated solutions the degree of dissociation is very low. Concentrated sulphuric acid, for example, is practically a non-conductor, although a dilute solution of the same possesses a relatively high conductivity.

The ease with which a current can pass through a cell containing two electrodes immersed in an electrolyte depends then upon the distance by which the electrodes are separated, and upon the number and nature of the ions which are between them.

The resistance of the cell may be decreased in a variety of ways. For example, a substance possessing a high degree of dissociation may be added to the solution, and, provided that it does not materially influence the degree of dissociation of the substance already present, the number of ions between the electrodes will be accordingly increased, and thereby the conductivity of the solution. The solution may also be warmed. The effect of this is generally to slightly increase the degree of dissociation, but more especially to decrease the viscosity of the solvent, as a result of which the ions experience less resistance to their movements through the solution, and the passage of the current is thus expedited. Another means at hand is to diminish the distance between, or to increase the size of, the electrodes. The effect of the former is readily understood, and by the latter a greater number of ions are brought within the sphere of action.

A word more as to the influence of ions themselves. Since the electricity is transported by the ions, the rate of migration of the same must be an important factor of the conductivity. Hydrogen of all ions has the highest velocity of migration. Accordingly all highly dissociated acids are good conductors. The hydroxyl ion comes next, which explains the relatively high conductivity of the bases. The conductivity of a solution is indeed nothing more than a function of the rates of migration of the cathion and anion.—*Trans.*]

THEORY OF ELECTROLYTIC PRECIPITATION.

When viewed from the standpoint of the theory of electrolytic dissociation the processes of quantitative electrolysis may be generalized as follows. Quantitative determinations may be divided into two classes according to whether the determination of a cathion (metal) or an anion (halogen or

metal peroxide) is concerned. What takes place in the former case is evident without further explanation. The metal ions migrate in the direction of the positive current, to the cathode; discharge, and separate on the electrode in the form of a smooth metallic coating. The halogens may be separated in a similar manner; but since some of them are gaseous or liquid, it is not practical to weigh them directly. Instead, therefore, of using inert platinum electrodes as are used with metals, silver electrodes are employed. With these the halogen atoms combine, at the moment of discharge, to form halogen silver compounds which adhere firmly to the electrode. The increase in weight of the electrode gives directly the quantity of the halogen which has separated.

The process in the separation of metal peroxides (only lead and manganese peroxides will be here considered) is somewhat more complicated. Formerly the formation of PbO_2 and MnO_2 was attributed to an oxidation brought about by the electrolytically generated oxygen. The investigations of Liebenow* and Löb† have made it appear that lead peroxide ions and manganese peroxide ions are already present in the solutions. Since the peroxides separate from strong nitric acid solutions, it must be assumed that through the oxidizing power of this acid oxygen ions are formed in the solutions, and that these combine with the lead or manganese ions to form peroxide ions. Since in the peroxides of the bivalent metals the two positive charges of the metal are combined with the four negative charges of the two oxygen atoms, the resulting peroxide ion therefore possesses two negative charges and consequently behaves like a bivalent anion. It is precipitated on the positive electrode as a smooth, adherent coating

* Zeitschr. f. Electrochemie, 1895–96, pp. 420, 653.

† Zeitschr. f. Electrochemie, 1896–97, p. 100.

in a form similar to that of a metal. The details of the reactions will be given in the Special Part.

From what has been said, the necessity of accurate data in the performance of electro-analyses is obvious, for unless all the important conditions are determined and recorded the experiment cannot be accurately repeated.

Since the determination of the resistance of the liquid in the cell is beyond the scope of analytical work, therefore, instead of this, the exact volume and composition of the solution, as well as the size and shape of the electrodes, must be stated. In addition to this the tension at the electrodes, the current strength as read directly on the amperemeter, and the calculation of the current density from the current strength, for the electrode on which the quantitative precipitation has taken place, must be given. All electrical relations are influenced by the temperature, so that an exact knowledge of this is most essential. The length of time required for the electrolysis and the nature of the source of current having been specified, all adequate and necessary data are at hand to enable every one to repeat the analysis under exactly similar conditions.

DETERMINATION OF THE CURRENT MAGNITUDES.

1. MEASUREMENT OF THE CURRENT STRENGTH.

The current strength is measured either by means of the chemical or the electromagnetic action of the current. The chemical instruments are the oxyhydrogen gas voltameter and the weight voltameter ; the first of which depends upon the volume of gas produced, the second upon the weight of metal precipitated.

THE OXYHYDROGEN GAS VOLTAMETER.

The construction of the apparatus is shown in Fig. 1. The cylindrical vessel g is partly filled with pure dilute 33

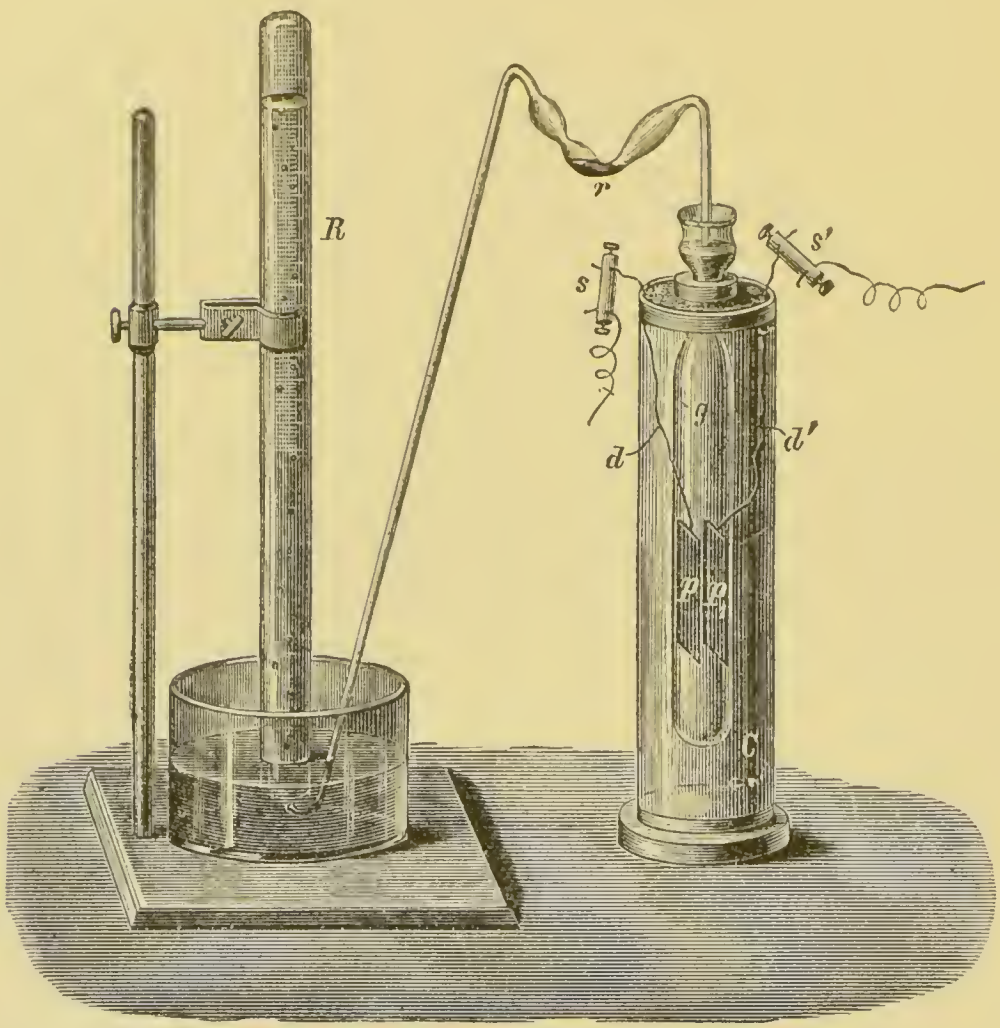

FIG. 1.

per cent sulphuric acid. The platinum wires d and d' welded to the platinum strips p and p_1* are fused into the walls of the vessel g. This latter stands in a large cylinder C of water which serves to cool it. The platinum wires end in the screws

*In the apparatus used by the author, the platinum electrodes are 31 × 13 mm., and are distant from each other 20 mm.

s and s', which are connected with the battery. The oxyhydrogen gas, as it is formed, passes through the tube r, which contains a little water, and is then collected in the measuring-tube R, which is graduated into $\frac{1}{10}$ cc. and filled with water. To measure an electric current with the voltameter, the water over which the gas is collected is first saturated with oxyhydrogen gas, and then, by the use of a watch with second-hand, the volume of gas is observed which the current yields in a minute, or, if the current is weak, in a longer time. To compare observations, the volume should be reduced to 0° and 760 mm. pressure.

v = observed volume of oxyhydrogen gas;
v_1 = normal volume (at 0° and 760 mm.);
t = observed temperature;
h = pressure reckoned in mm. of mercury.

$$v_1 = \frac{v}{1 + 0.00367t} \cdot \frac{h}{760}.$$

Let l indicate the height of the column of liquid, s the density of the liquid, and b the barometric height; then

$$h = b - l\frac{s}{13.6}.*$$

The oxyhydrogen gas voltameter, which unfortunately is still frequently used, is quite unsuited to the purpose for which it is intended, since, among other disadvantages, it possesses a high tension which under some circumstances may be much greater than that of the experiment. In addition to this, the comparison of measurements made with different oxyhydrogen gas voltameters is only possible when the instrn-

* 13.6 sp. g. of mercury.

ments correspond absolutely with one another in construction, a condition not possible in practice.

THE WEIGHT VOLTAMETER.

The weight voltameter, which is used in the form of a copper or silver voltameter, has found quite as little application in electrolytic laboratories. Its construction is given in Fig. 2.

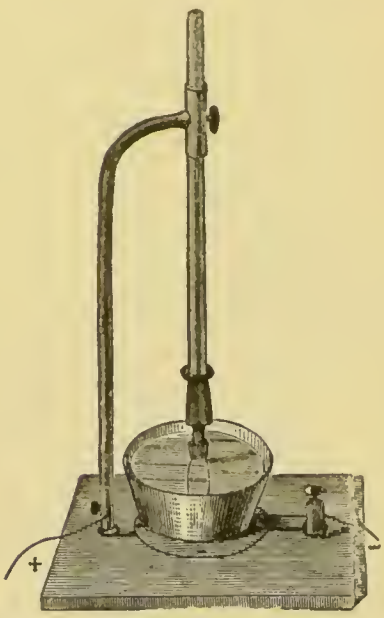

FIG. 2.

Both methods have been supplanted by the electromagnetic measuring instruments, some of which make use of the deflection of the magnetic needle caused by the current, and others of the magnetic properties induced in a soft iron core. To the former class belong the sine and tangent galvanometers; to the latter, the instrument most used in practice, i.e., the amperemeter.

THE TANGENT GALVANOMETER.

In the tangent galvanometer (Fig. 3) there is a small magnet which has its plane of swing horizontal and at right angles to the plane of a ring shaped circuit. The actual position of the magnet when at rest, as well as that of the plane of the windings of the circuit, is the magnetic meridian. When a current flows through the wire ring, there results a deflection of the magnetic needle, the amount of which depends upon the strength of the current and the number of windings. If H denotes the horizontal component of

the earth's magnetic field, n the number of turns of wire in the ring, r the radius of the ring, and ϕ the angle of deflection

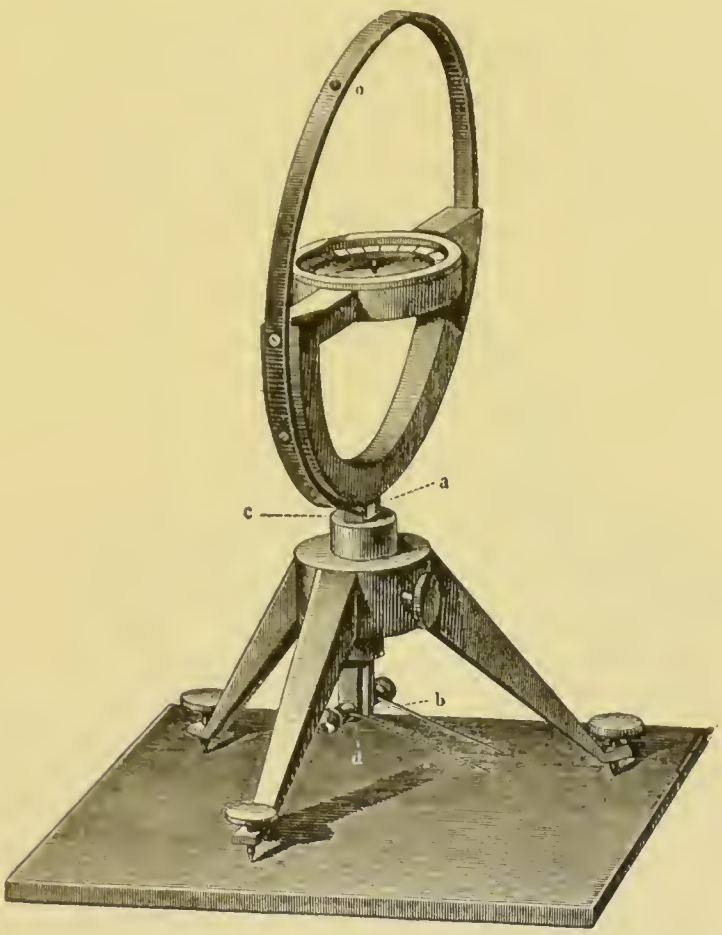

FIG. 3.

caused by the current, then the current strength

$$C = \frac{r}{2\pi \cdot n} H \cdot \tan \phi.$$

$\frac{r}{2\pi \cdot n}$ is a constant for each instrument, which may be determined by connecting it with a source of known current strength, according to the equation

$$\frac{r}{2\pi \cdot n} = \frac{C}{H \cdot \tan \phi} = K.$$

The current strength to be determined may then be easily found; it is $C = K \cdot H \cdot \tan \phi$.

THE SINE GALVANOMETER.

The sine galvanometer (Fig. 4) differs from the tangent galvanometer in that the plane of the windings is not fixed in the meridian, but is turned in the direction of the needle dis-

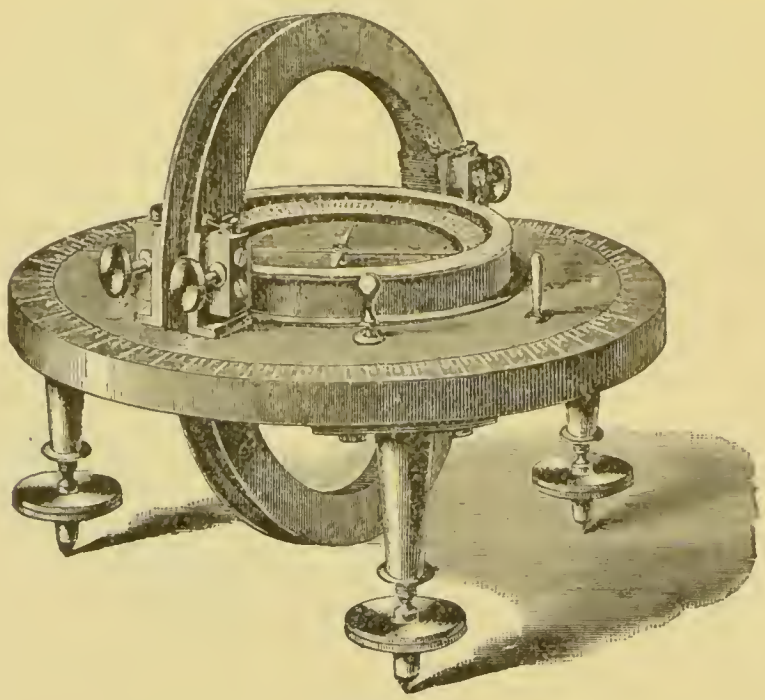

FIG. 4.

placed by the current, until the position of the latter again corresponds with the plane of the circuit. The angle through which the current circle has been turned from its original position in the magnetic meridian is then read off. The current strength is

$$C = K \cdot H \cdot \sin \phi,$$

where K denotes the constant reduction factor of the instrument.

OTHER FORMS OF GALVANOMETERS.

The galvanometers which are used for making the most accurate measurements depend likewise upon the displacement

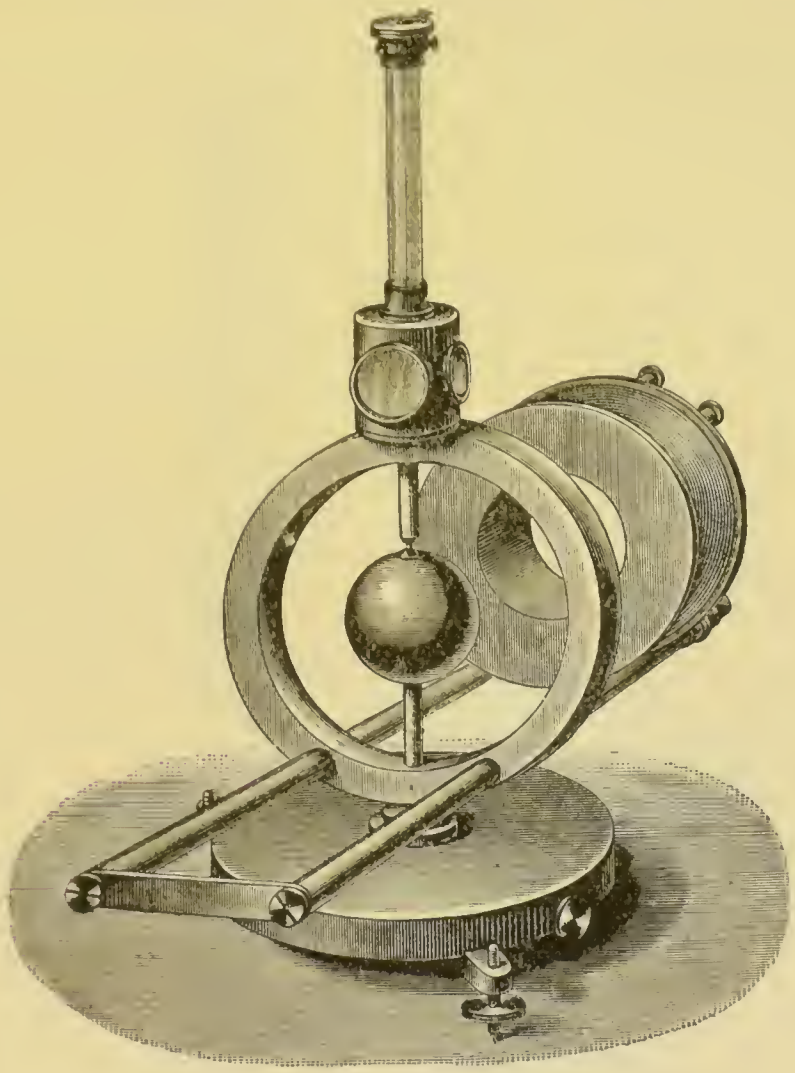

FIG. 5.

of the magnetic needle by a circular current. Here, however, the needle is suspended by a fine cocoon fiber, between spools containing a very large number of turns of wire. In order to remove the magnet from the influence of the earth's magnetism, a pair of so-called astatic needles are frequently em-

ployed. Two exactly similar magnets are rigidly connected with one another, so that the north pole of the one is situated exactly over the south pole of the other, and correspondingly the south pole of the first above the north pole of the second. By this arrangement the effect of the earth's magnetism is neutralized by the two needles.

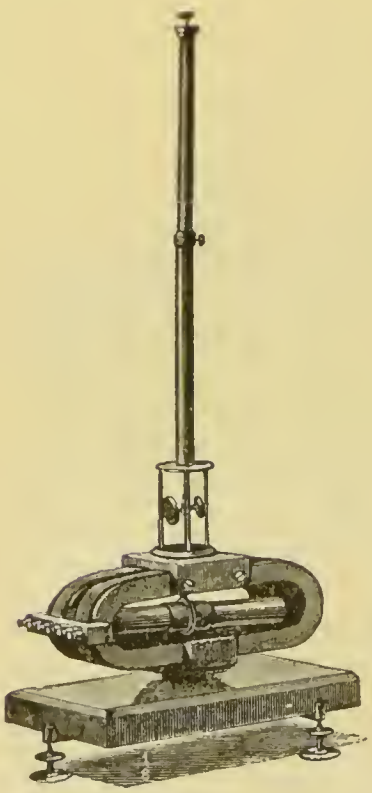

FIG. 6.

FIG. 7.

The angle of displacement is read by means of a telescope and a mirror which swings with the needle. The scale, which is rigidly clamped to the telescope, shows the divisions which correspond to the deflection of the needle.

Figures 5 and 6 show two practical galvanometers.

The effect of the magnetism induced in a soft-iron core is made use of in the two instruments, most useful for electrol-

ysis; the Kohlrausch spring galvanometer and the amperemeter (often called ammeter).

THE SPRING GALVANOMETER.

In this apparatus of Kohlrausch (Fig. 7), a hollow cylinder of sheet iron is suspended within a vertical solenoid by a spiral spring. When a current is passed through the instrument, the iron cylinder is drawn down into the solenoid until the force of attraction is equalized by the tension of the spring. A small pointer attached to the spring moves over a scale which is empirically graduated and gives the current strength directly in amperes.

THE AMPEREMETER.

In the amperemeter (Fig. 8) the solenoid is usually placed horizontal and carries eccentrically a bent piece of thin sheet

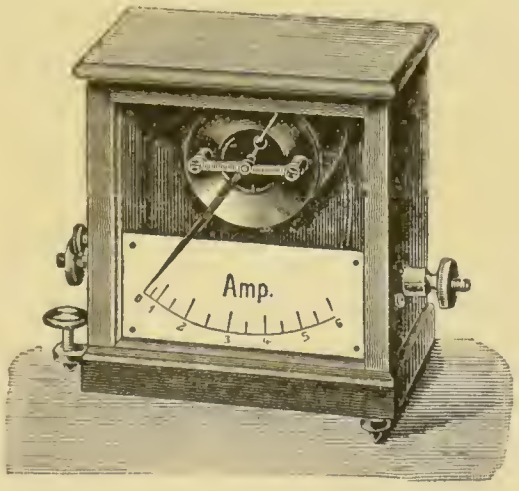

FIG. 8.

iron which is provided with a long pointer. This pointer moves over a scale. These instruments under suitable conditions are extraordinarily sensitive.

2. MEASUREMENT OF THE TENSION.

For measuring the tension a great number of instruments are in use, the application of which depends upon the fineness of the measurement which is to be carried out. Two instruments are employed in electrolysis, the voltmeter and the torsion galvanometer, while for exact determinations of differences of potential, especially small ones, the Lippmann capillary electrometer and the quadrant electrometer, lately in the form improved by Nernst, have been generally adopted.

THE VOLTMETER.

Since, according to Ohm's Law, $E = C \cdot R$, every measurement of tension may be referred to a measurement of the current strength provided that the resistance R remains constant. This is done in the voltmeter, which has the external form of an amperemeter, by giving the solenoid a very high resistance, 1000 ohms for example. In this way, the resistance of the connecting wire may be left out of consideration, and the fall in tension is confined practically to the coils of the solenoid alone. Further, the voltmeter is always connected on a shunt circuit.

If the resistance in this shunt is low, then the greater part of the current passes through it, causing a fall to take place in the tension at the cell under measurement. The corresponding value obtained for the tension will therefore be too low.

If, however, the resistance of the voltmeter is very high, then the current will pass through the cell with almost unaltered tension and only an extremely small fraction will go through the measuring instrument itself. The scale is so

constructed with reference to the resistance that the amperes are converted directly into volts, according to the equation, which for the solenoid mentioned would be

$$E = 1000 \cdot C.$$

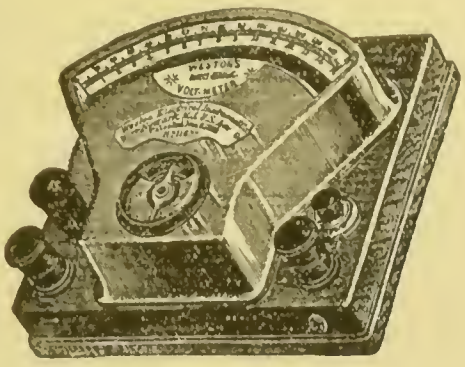

Fig. 9.

A most excellent form of apparatus is the voltmeter of Weston (Fig. 9). This gives the value accurately to $\frac{1}{10}$ volt and allows of approximation to $\frac{1}{100}$ volt. A mirror, placed below the scale over which the pointer moves, prevents parallax in reading.

THE TORSION GALVANOMETER.

The principle of this instrument is electromagnetic. A light bell magnet swings between two parallel and perpendicular coils containing many windings of wire. These two spools are so connected with one another that the current flowing through each of them tends to deflect the magnetic needle in the same direction. The magnet, the swinging of which is usually retarded by copper damping, is suspended from the cover of the case by a spiral spring. To this spring a horizontally moving pointer, which is just beneath the glass cover of the instrument, is attached. A second pointer is fastened directly to the magnet.

The instrument is used as follows: By revolving the case the needle is brought into the magnetic meridian, so that the two pointers correspond to the zero point of the scale on the glass cover. Care must be taken that the magnet swings entirely free, which is insured by setting the instrument exactly horizontal by means of the foot-screws. If the

binding-screws of the galvanometer are now connected with the source of current or with the cell, the tension of which is to be determined, the magnet will be deflected from its position of rest and the pointer attached to the spiral spring must be turned a certain distance in order to bring the pointer rigidly connected to the magnet back to the zero point on

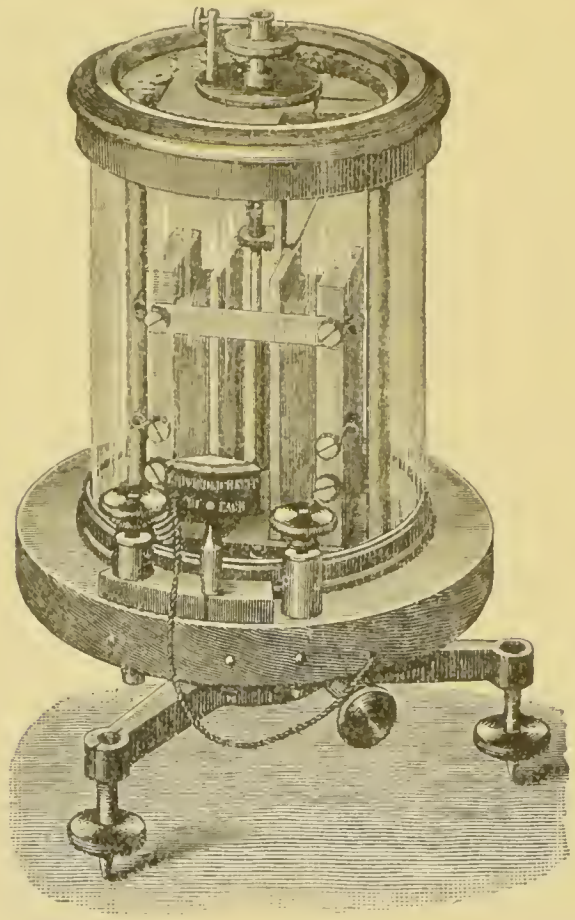

Fig. 10.

the scale, and thereby to return the magnet itself to its former position. In this operation the pointer fastened to the top of the spiral spring has been moved through a certain number of divisions on the scale, and this scale is empirically calibrated, so that by the position of the pointer the tension is given in $\frac{1}{100}$ volt. By interposing resistance, the sensitiveness may be

so decreased that the divisions correspond to tenths or to whole volts. Fig. 10 shows a torsion galvanometer of the type manufactured by Siemens & Halske (Berlin).

The principle of the construction of the instrument is similar to that of the voltmeter. The deflection of the needle is of course proportional to the current strength, but since the resistance of the spool windings is very high and remains constant, a strict proportion exists between the intensity and the tension, so that the direct reading in volts is made possible by the use of the equation

$$E = k \cdot C.$$

THE LIPPMANN CAPILLARY ELECTROMETER.

This instrument is chiefly employed in the measurement of electromotive forces by the Poggendorf compensation method, most practical in the arrangement described by Ostwald.

In this a known electromotive force is opposed to the one which is to be measured, and the former is modified through alterations of the resistance by certain known amounts, until the two electromotive forces are equal and compensate one another.

In practice, an element of known electromotive force is so connected with a resistance-box, which contains for example 1000 ohms, that the whole fall in potential takes place through the 1000 ohms. Every resistance of 10 ohms is provided with a clamp to which a wire may be connected. If the known electromotive force is for example 1 volt, this will be distributed over the resistance in such a way that the 1000 ohms will represent a fall of 1 volt, every 100 ohms one of 0.1 volt, and every 10 ohms one of 0.01 volt. The electromotive force to be measured is now connected with the

two clamps of the resistance-box in such a manner that it will be opposed to the known electromotive force and the resistance between the two clamps is varied, until the two electromotive forces are equal and compensate one another. If, for example, the resistance between the clamps is 100 ohms, then the electromotive force to be measured is equal to 0.1 volt, for 110 ohms it would be 0.11 volt, for 120 ohms 0.12 volt, etc.

In order to determine when the electromotive force which is being measured is equal to the opposed electromotive force, a Lippmann electrometer of the form given by Ostwald * is employed. (Fig. 11.)

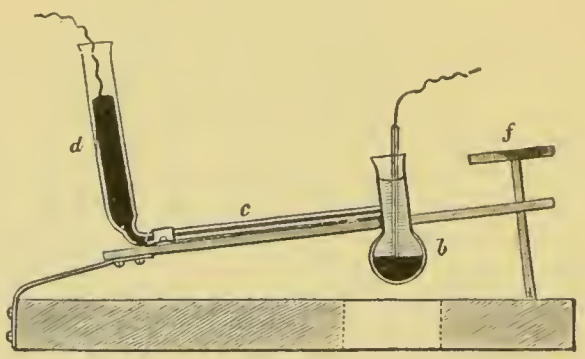

FIG. 11.

"A platinum wire, partly encased in a glass capillary, leads from an insulated binding-screw and extends into the mercury at the bottom of the bulb *b*, which also contains above the mercury a 10 per cent sulphuric acid solution. The capillary tube *c* opening into the bulb *b* is filled in its upper part with acid; its lower part contains mercury, likewise the tube *d*, which is in connection with a second binding-screw. The position of the mercury in the capillary tube *c* may be regulated through altering the inclination of the capillary by means of the screw at *f*. That this apparatus may

* Ztschr. f. phys. Chem., 1890, p. 471.

give satisfactory results it should be short-circuited just before use, and consequently it was connected with a switch so constructed that on breaking the current the electrometer was always short-circuited, and on making the current this connection within itself was destroyed. In measuring electromotive forces, so much of the resistance of the box was brought between the movable clamps that the mercury remained at rest on closing the circuit. A millimeter scale placed beneath the capillary, and a lens above it, aided in the reading. It was possible to approximately estimate to a thousandth volt. One hundredth volt corresponded to $3\frac{1}{2}$ divisions on the scale."

The Lippmann capillary electrometer, the theory of which cannot be entered upon here, depends upon the fact that the surface tension of mercury alters under varying electrical conditions. When the two opposed electromotive forces are equal, then the mercury is electrically neutral and the meniscus returns to its normal position.

THE QUADRANT ELECTROMETER.

The quadrant electrometer, which was constructed in the most varied forms by W. Thomson and is very generally used for the measurement of potentials, has the following general construction.

Four separated sectors of a flat, cylindrical metal box rest upon four insulating glass supports. Each of these sectors is called a quadrant. Each pair of oppositely located quadrants is in metallic connection. Within the hollow space formed by the four quadrants the so-called needle, a thin, horizontal plate of aluminium, is suspended by a fine wire which also carries a mirror for reading. A wire leads from the needle to a vessel filled with sulphuric acid, situated beneath the quadrants.

In using the instrument, the aluminium needle is charged to a comparatively high potential by connecting it with some

source of electricity, usually a Leyden jar, through the wire dipping into the sulphuric acid. One pair of quadrants is then grounded, and the other pair is connected to one pole of the electromotive force to be measured, the second pole of the electromotive force being connected with the earth. So long as all the quadrants have the same potential, the aluminium needle remains at rest; the difference between the potential of the earth and the one under consideration is determined from the deflection of the needle measured by means of the mirror and scale.

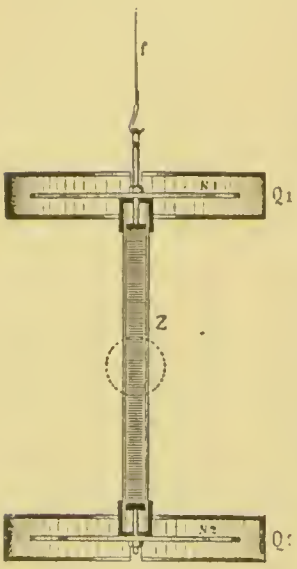

FIG. 12.

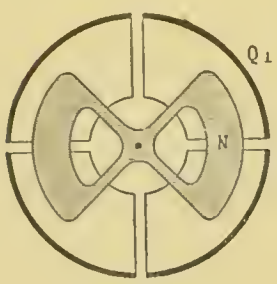

FIG. 13.

Nernst and Dolezalek * have made the employment of this instrument more simple and accurate. They avoid the operation of charging the aluminium needle before use, by employing a small perpendicularly hung Zamboni pile having a tension of about 1400 volts. (Figs. 12 and 13.)

A small Zamboni pile Z, suspended by the quartz fiber f, has fastened to its two poles the electrometer needles N_1 and N_2, which swing in the quadrant boxes Q_1 and Q_2, placed one above the other.

The measurement of a difference of potential is carried out by comparing the instrument with a normal tension, or by the compensation method.

SOURCES OF CURRENT.

Two classes of current supply are employed in electrolysis, chemical and physical. The first class is represented by the

* Ztschr. f. Electrochemie, 1896-97, p. 1.

galvanic elements, which are further divided into primary and secondary elements, according as the difference of potential is directly due to a chemical reaction or to a polarization current (accumulators).

To the second class belong the electromagnetic machines and thermopiles. The most important apparatus will be briefly described in the following section.

1. PRIMARY GALVANIC ELEMENTS.

LECLANCHÉ CELL.

This is a one-fluid cell using a solution of ammonium chloride, which surrounds the negative pole, the zinc. The

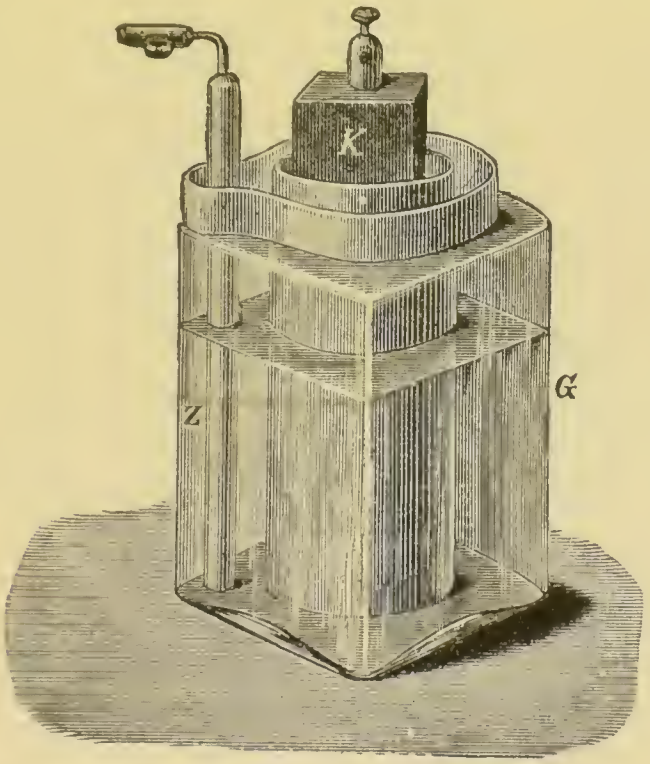

FIG. 14.

cell is much used in the form shown in Fig. 14. In the jar, which is square in section, with a rounded projection at

one corner, stands a porous clay cup, from which projects a block of carbon K surrounded by coarsely pulverized manganese dioxide, or a mixture of manganese dioxide and retort carbon. In the projecting rounded corner is a stout rod Z of amalgamated zinc. The carbon and zinc are both provided with binding screws, and are immersed in a concentrated solution of ammonium chloride.

Leclanché also uses, in place of the powdered manganese dioxide, compressed prisms (shown in Fig. 15) con-

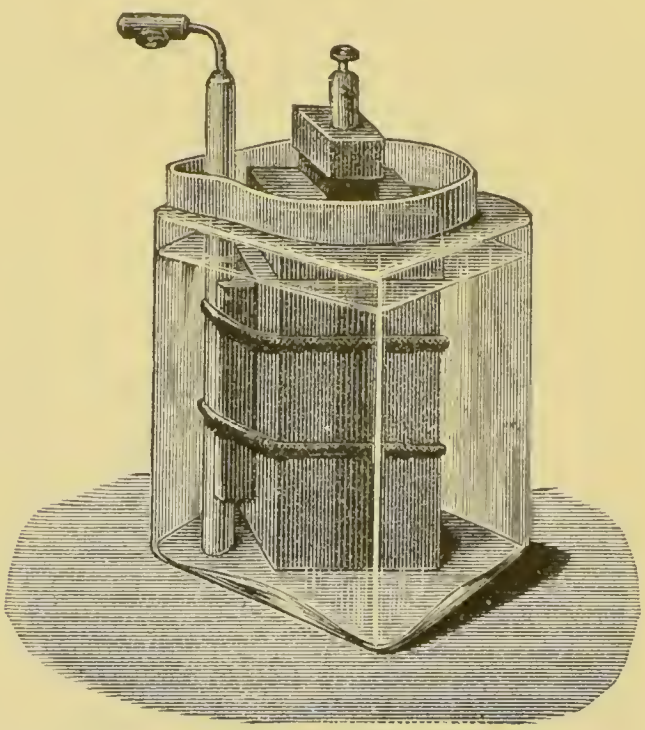

Fig. 15.

sisting of 40 parts manganese dioxide, 55 parts gas carbon, and 5 parts shellac; a little potassium sulphate is also added to increase the conductivity. The porous cup is thus dispensed with. This cell has an electromotive force of 1.48 volts.

MEIDINGER CELL.

In contrast to the Leclanché cell, that of Meidinger contains two liquids, solutions of magnesium and copper sulphates. The element is constructed as follows: In the glass vessel G (Fig. 16) stands a smaller glass g, and in this a copper cylinder K to which an insulated copper wire D is fastened.

A second cylinder Z of zinc, to which the projecting wire D_1 is fastened, is placed in the upper part of the vessel G. The balloon-shaped glass B, filled with crystals of copper sulphate, closes the cell. The cell is filled to about three-fourths of its capacity with a solution of 1 part crystallized magnesium sulphate in 7 parts of water; and the balloon-shaped flask containing copper sulphate is filled up with water, closed with a stopper fitted with the glass tube r, and, as the cut shows, inverted in the cell.

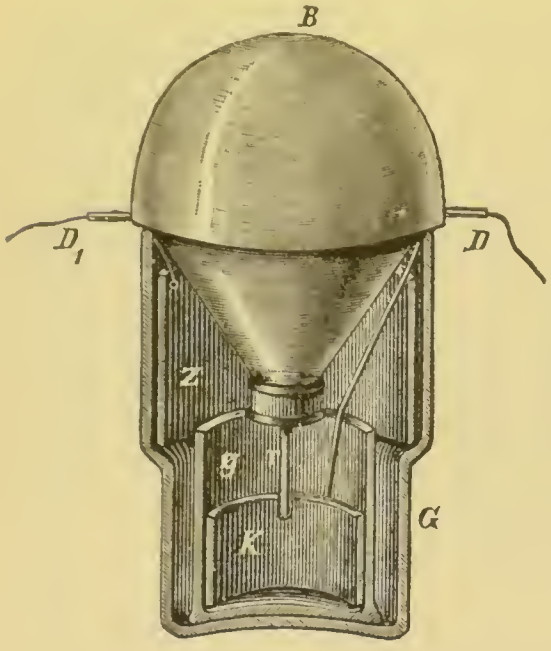

FIG. 16.

Electromotive force about 1 volt.

DANIELL CELL.

In a jar of glass (Fig. 17) is a porous clay cup T, and in this a cylinder of cast zinc, the negative pole (Fig. 18). The

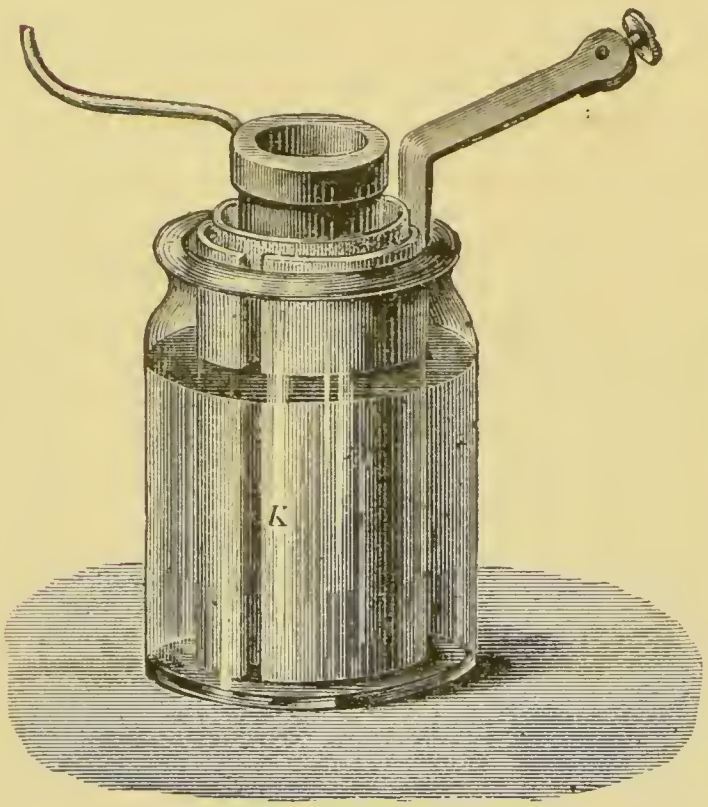

Fig. 17.

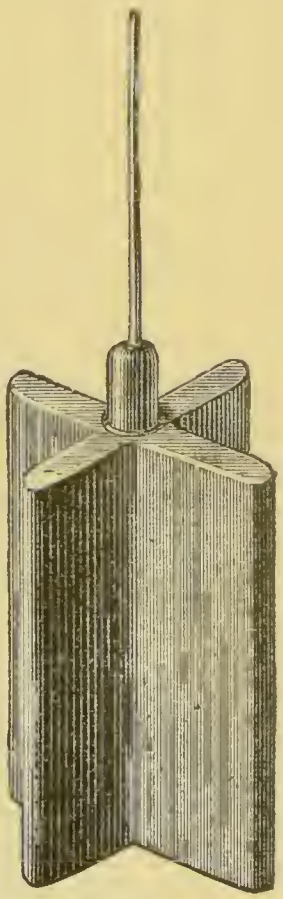

Fig. 18.

porous cup is surrounded by a cylinder of sheet-copper K, the positive pole.

The cylinder of amalgamated zinc * stands in dilute sul-

* The zinc is easily amalgamated by plunging it into mercury, on the surface of which a little hydrochloric acid has been poured. The amalgamated cylinder is then placed in a vessel of water to remove the hydrochloric acid, and allow the excess of mercury to drop off.

phuric acid (1 : 20), and the copper cylinder in a solution of copper sulphate ; the sulphuric acid may be replaced by a solution of zinc sulphate.

The element has an electromotive force of 1.079 volts.

[The modification of the Daniell cell known as the gravity cell is the form commonly in use for telegraph batteries in this country, and is the cheapest and most convenient cell for constant batteries to yield currents of moderate strength in scientific laboratories. It is very generally thus used. The copper is placed at the bottom of the jar; an insulated copper wire is riveted to it, long enough to pass up through the solutions and connect with a binding screw on the zinc of an adjacent cell, or with the wire which serves to conduct the current to the solution for electrolysis. The bottom of the jar, about the copper, is filled with copper sulphate; the zinc, a heavy casting with large surface, is suspended a few inches below the top; and the jar is filled with water sometimes acidulated with sulphuric acid. After standing a few hours, the copper sulphate dissolves; copper is precipitated, and zinc dissolved; and the jar, in its normal working state, thus contains two solutions; the heavier, of copper sulphate, below, and the lighter, of zinc sulphate, above. The porous cup of the Daniell cell is thus dispensed with, and the zinc does not require amalgamation.

The cut (Fig. 19) shows one of the simplest gravity cells, having the zinc in the so-called "crow-foot" shape, hanging directly on the edge of the jar, and furnished with a binding-screw.

The outfit of the chemical laboratory of the Pennsylvania State College, while under the translator's charge, was found

convenient, and sufficient for the needs of an ordinary laboratory for instruction. Some twenty "crow-foot" gravity cells were kept in working condition, and eight Grove cells could be set up if needed for a strong current. Four sets of connecting-wires were run from the battery-room to the laboratory desk set apart for electrolytic work, each set being so arranged with binding-screws as to be quickly connected with any desired number of cells. (See under "Secondary Batteries," p. 47.) — *Trans.*]

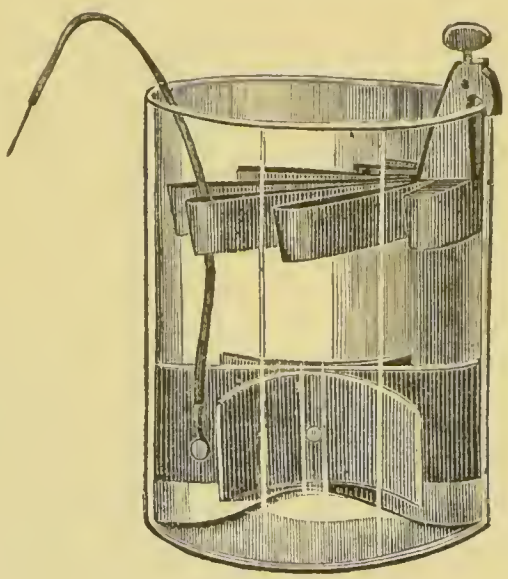

Fig. 19.

GROVE CELL.

The positive pole is a sheet of platinum foil of the form shown in Fig. 20 ; this is placed in a porous cup filled with nitric acid. The negative pole is a cylinder of amalgamated zinc placed in a glass jar containing dilute sulphuric acid (1 : 20). Fig. 21 shows the arrangement of the cell.

Electromotive force 1.81 volts.

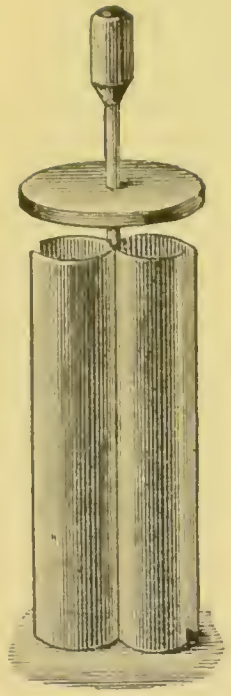

Fig. 20.

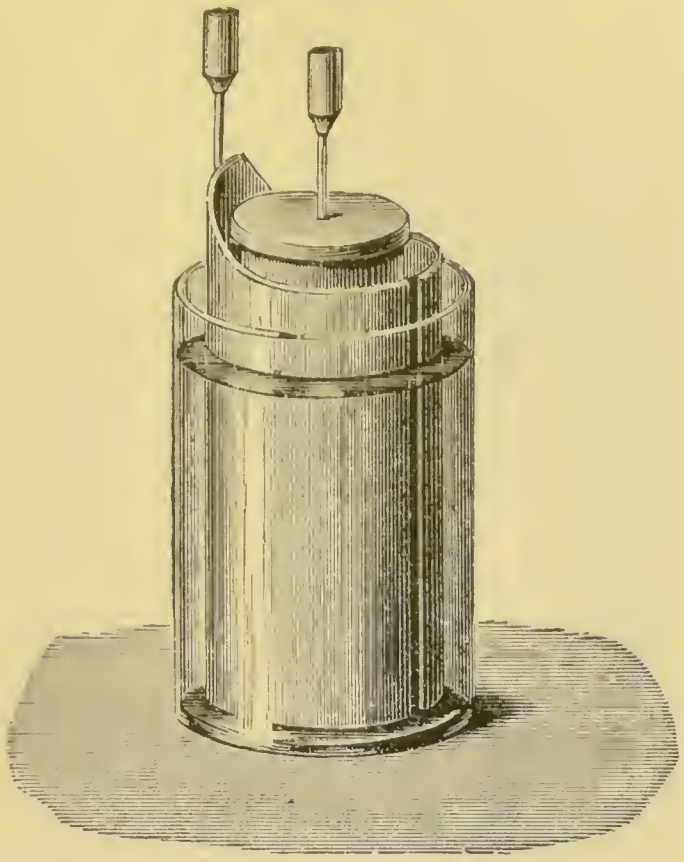

Fig. 21.

BUNSEN CELL.

In the Bunsen cell, the platinum is replaced by a prism of retort carbon (Fig. 22) standing in a porous cup filled with nitric acid. The negative electrode, as in the Grove cell, is a cylinder of amalgamated zinc placed in a glass jar filled with dilute sulphuric acid (1 : 20). The screw-clamp shown in Fig. 23 is often used to fasten a metallic connection to the carbon prism. It has, however, the disadvantage that the clamp is quickly oxidized by the decomposition products of the nitric acid, and the contact thus broken. It is better, therefore, to insert in the carbon a metallic socket (Fig. 24), the stem of which is closely covered with platinum foil.

Fig. 25 shows the Bunsen cell in its most common form. Electromotive force 1.80 volts.

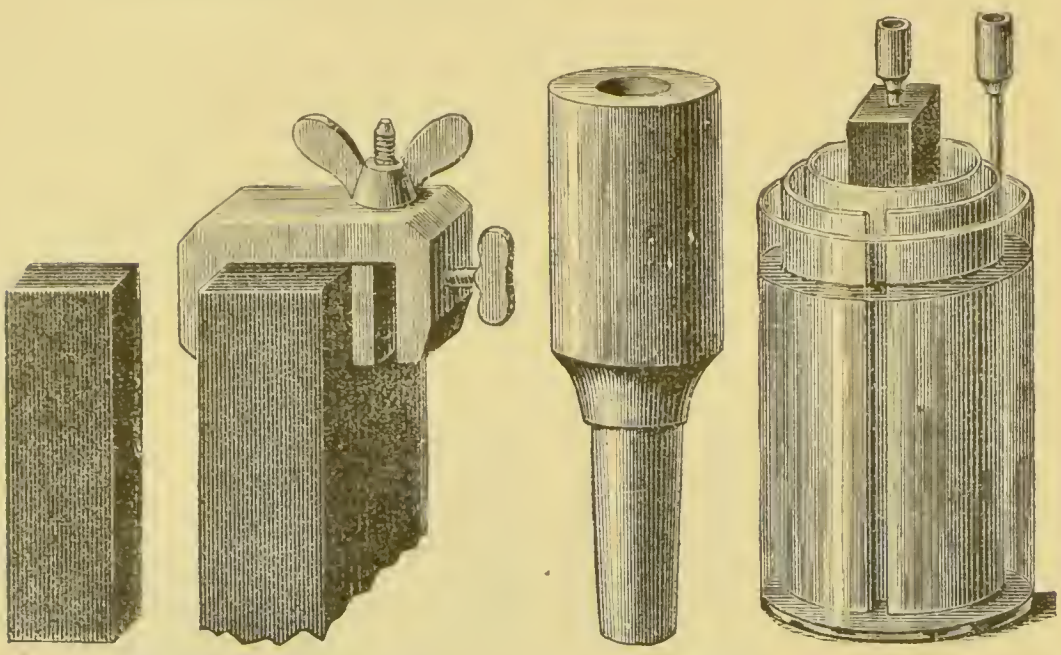

FIG. 22. FIG. 23. FIG. 24. FIG. 25.

CUPRON ELEMENT.

A copper oxide plate and a zinc plate dip into an aqueous sodium hydroxide solution, as shown in Fig. 26. When a current is produced the following reactions take place:

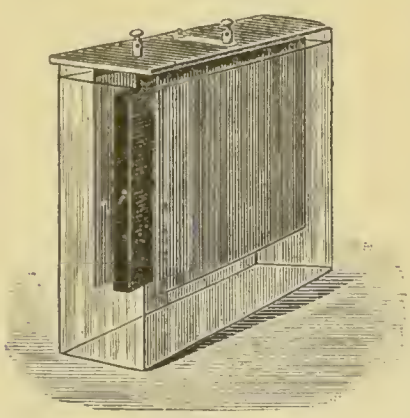

FIG. 26.

I. $Zn + 2NaOH = Zn(OH)_2 + 2Na.$

II. $CuO + 2H = Cu + H_2O.$

The current ceases as soon as all the copper oxide is reduced or all the zinc is dissolved. In the type introduced on the market by Umbreit & Matthews (Leipzig), when the copper oxide plate has been

reduced it may be reconverted into copper oxide by allowing the plate to stand for 15 hours in a warm place.

The element has an electromotive force of 0.8 volt, with an internal resistance of 0.05 ohm.

[EDISON-LALANDE ELEMENT.

This element, having a form differing somewhat from the above cupron element, but depending for the production of the current upon a similar chemical reaction, has come largely into use in the United States.

FIG. 27.

Elements of this type, with capacities of from 50 to 600 ampere-hours, are manufactured, and furnish a very convenient primary source of electricity. (Fig. 27.)]

GALVANIC SECONDARY ELEMENTS.

(ACCUMULATORS, OR STORAGE BATTERIES.)

While the primary elements previously described furnish electrical energy through chemical reactions which involve a gradual using up of their component parts, the characteristic of accumulators lies in the fact that by passing an electric current through them they are brought into a condition which makes it possible for them to furnish a polarization current, and thereby to return to their original condition. Elements of this class are called reversible elements.

Accumulators are therefore instruments which alternately convert chemical energy into electrical energy, and electrical energy into chemical energy.*

The principle of their construction depends upon the behavior of lead plates in dilute sulphuric acid on the passage of a current. If we have two such plates dipped in sul-

* Elbs, Die Akkumulatoren, 1896.

phuric acid, one serving as cathode, the other as anode, it will be observed, upon closing the current, that a brown coating forms upon the positive electrode, spongy lead separating out at the same time on the negative plate. This phenomenon is due to the formation, at both poles, of a saturated solution of lead sulphate, the lead ions of which discharge upon the cathode as spongy lead, while at the anode the lead and oxygen ions separate in the form of lead peroxide. If the primary current be broken and the polarization current allowed to discharge by establishing metallic connection between the two plates, the following reaction takes place: The sulphuric acid dissolves the spongy lead at the negative pole; the hydrogen ions thus made available migrate to the anode with their positive charges and reduce the lead peroxide there present to lead oxide, which again forms lead sulphate with the sulphuric acid. As soon as all the spongy lead is dissolved and all the lead peroxide is reduced, the polarization current ceases, the accumulator is discharged, and the original condition is again reproduced. By means of a new primary current (charging current) the accumulator may be again brought into an available condition.

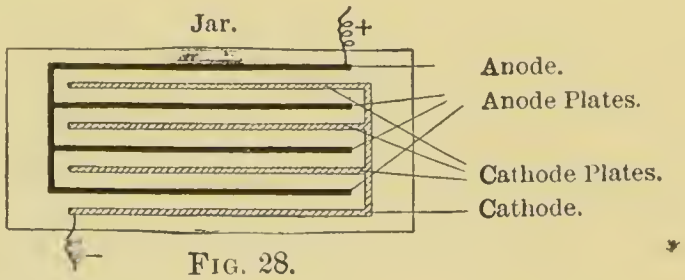

FIG. 28.

In the construction of accumulators, the longest possible continuation of the polarization current is aimed at, together with the lowest possible internal resistance of the element. The electromotive force between lead and lead peroxide in dilute sulphuric acid is approximately 2 volts. In order to

arrive at the most practical construction, a number of parallel plates are metallically connected together and hung as cathodes in a trough containing sulphuric acid. Similarly, an equal number of anode plates are hung in and so arranged that each cathode plate is between two anode plates and *vice versa*, each anode between two cathode plates. (Fig. 28. View from above.)

The time required for charging depends upon the area of the plates and the condition of the spongy lead and lead peroxide. In order to satisfy all requirements the so-called

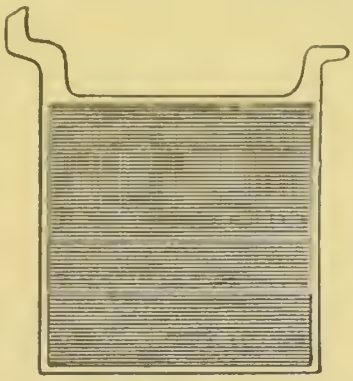

FIG. 29.

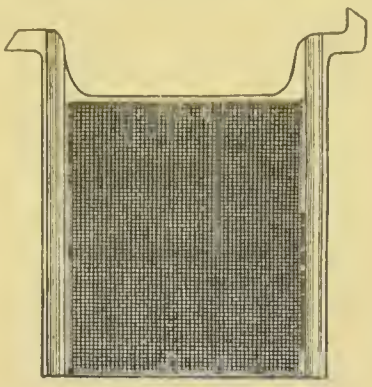

FIG. 30.

"active material" (i.e., the spongy lead and lead peroxide) is attached to a solid lead frame by the employment of a series of processes ("forming," etc.), which cannot be discussed here. Fig. 29 shows a negative, Fig. 30 a positive plate, while Fig. 31 gives an accumulator of the form commonly used.

The first experiments with accumulators for the purposes of quantitative analysis were conducted in the Aachen laboratory, with apparatus especially constructed by Professors Farbaky and Scheneck * in Schemnitz (Hungary).

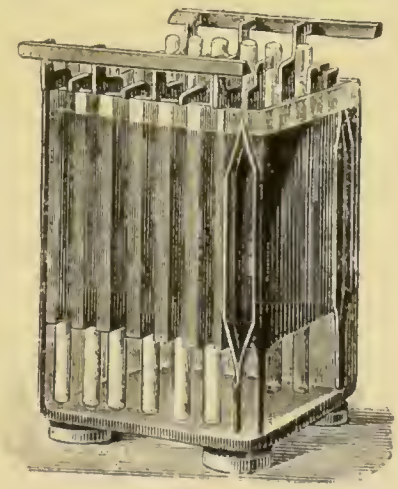

FIG. 31.

* Compare Ueber die elektrischen Akkumulatoren von Farbaky und

These gentlemen had the kindness to place two accumulators at the author's service for testing, and he made his first experiments in 1888, working with R. Schelle, at that time professor in the Schemnitz Royal School of Mines. These accumulators have 6 negative and 5 positive lead-plate electrodes, each 6 mm. thick. The weight of the electrodes is 15.5 kg., the volume of the 33% sulphuric acid 3.5 l., the total weight of each cell 35 kg. The active surface of the electrodes is 3133 sq. cm., so that the internal resistance is very low, measuring between 0.0166 and 0.017 ohm. The accumulators can be charged at a 20 to 25 ampere rate, and yield in discharge at 23, 30, 40, and 60 ampere rates respectively 150, 148, 140, and 125 ampere-hours, with a fall of not over 10% in the voltage. If the discharge is lighter, and the fall in the electromotive force less than for lighting purposes, as in electrolytic analyses, an accumulator may yield over 250 ampere-hours.

Two such accumulators were fully charged, until OH gas was obviously disengaged, by a current of 20 to 25 amperes from the dynamo. The current was measured by a Kohlrausch galvanometer, made by Hartmann & Braun, Bockenheim, Frankfurt a. M., the scale of which read from 0 to 60 amperes. A second Kohlrausch amperemeter, divided from 0 to 15 amperes, was used to measure the current taken from the accumulators for the analyses.

A Siemens torsion galvanometer showed a tension, for each charged accumulator, of 2.05 volts.

By the use of these two accumulators, four to eight analyses were carried on simultaneously, and the accumulators kept in

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Scheneck (Dingler polyt. Journ., 257, 357); further, Bericht über die Akkumulatoren von Farbaky und Scheneck von A. v. Waltenhofen. Zeitschr. f. Elektrotechnik, 1886.

constant use day and night, except for the short intervals needed to change the solutions for analysis.

The results of analyses extending over a period of six days are subjoined.

First Day.

Tension 2.55 volts.

Determination of Copper from Nitric-acid Solution.

Taken $CuSO_4,5H_2O$.	Found Cu.
4.0140 g	1.0170 g = 25.33 %
4.1376 "	1.0480 " = 25.33
2.2340 "	0.5661 " = 25.34
2.3575 "	0.5978 " = 25.35

Tin from the Acid Ammonium Double Oxalate.*

Taken $SnCl_4 2NH_4Cl$.	Found Sn.
1.8450 g.	0.5964 g. = 32.33 %
2.0210 "	0.6548 " = 32.39

Antimony from Solution in Sodium Sulphide.†

Taken Sb_2S_3.	Found Sb.
0.2404 g.	0.1720 g. = 71.50 %
0.2551 "	0.1827 " = 71.60

* Classen's method: see Tin.
† " " " Antimony.

Second Day.

Tension 1.95 volts.

2.0490	g.	$NiSO_4 + (NH_4)_2SO_4, 6H_2O$	gave	0.3053	g.	Ni = 14.90%*
2.0180	"	" "	"	0.3000	"	" = 14.91
2.3400	"	$CoSO_4 + K_2SO_4, 6H_2O$	"	0.3440	"	Co = 14.70†
2.1200	"	" "	"	0.3120	"	" = 14.71
1.8920	"	$FeSO_4 + (NH_4)_2SO_4, 6H_2O$	"	0.2697	"	Fe = 14.25‡
2.1240	"	" "	"	0.3027	"	" = 14.25
1.0	"	$CuSO_4, 5H_2O$	"	0.2533	"	Cu = 25.33§
1.0	"	" "	"	0.2533	"	" = 25.33
1.0	"	" "	"	0 2534	"	" = 25.34
1.0	"	" "	"	0.2537	"	" = 25 37
1.9210	"	$SnCl_4 + 2NH_4Cl$	"	0.6219	"	Sn = 32.37‖
2.1320	"	" "	"	0.6900	"	" = 32.36

Third Day.

Tension 1.95 volts.

(*Six simultaneous analyses.*)

1.0050	g.	$CuSO_4, 5H_2O$	gave	0.2550	g.	Cu = 25.37%
1.0170	"	"	"	0.2580	"	" = 25.36
1.0006	"	"	"	0.2539	"	" = 25.37
1.0013	"	"	"	0.2540	"	" = 25.37
1.5680	"	$SnCl_4 + 2NH_4Cl$	"	0.5070	"	Sn = 32.34
2.4520	"	"	"	0.7946	"	" = 32.40

* Classen's method: see Nickel.
† " " " Cobalt.
‡ " " " Iron.
§ From the acid double oxalate, Classen's method.
‖ From the acid ammonium double oxalate.

Fourth Day.

Tension 1.95 volts.

1.0	g.	$CuSO_4,5H_2O$	gave	0.2532	g.	Cu = 25.32%
1.0	"	"	"	0.2535	"	" = 25.35
1.0	"	"	"	0.2532	"	" = 25.32
1.0	"	"	"	0.2536	"	" = 25.36
1.0	"	"	"	0.2535	"	" = 25.35
1.0	"	"	"	0.2538	"	" = 25.38
1.0	"	"	"	0.2539	"	" = 25.39
1.0	"	"	"	0.2537	"	" = 25.37
2.20	"	$NiSO_4+(NH_4)_2SO_4,6H_2O$	"	0.3277	"	Ni = 14 89
2.45	"	" "	"	0.3650	"	" = 14.89
2.1340	"	$CoSO_4+K_2SO_4,6H_2O$	"	0.3148	"	Co = 14.75
2.4350	"	" "	"	0.3587	"	" = 14.73

Fifth Day.

Tension 1.95 volts.

1.0	g.	$CuSO_4,5H_2O$	gave	0.2537	g.	Cu = 25.37%
1.0	"	" "	"	0.2537	"	" = 25.37
2.4120	"	$FeSO_4+(NH_4)_2SO_4,6H_2O$	"	0.3438	"	Fe = 14.25
2.2130	"	"	"	0.3156	"	" = 14.26

Sixth Day.

Tension 1.92 volts.

(*Eight simultaneous copper determinations.*)

1.0	g.	$CuSO_4,5H_2O$	gave	0.2533	g.	Cu = 25.33%
1.0	"	"	"	0.2534	"	" = 25.34
1.0	"	"	"	0.2536	"	" = 25.36
1.0	"	"	"	0.2533	"	" = 25.33
1.0	"	"	"	0.2537	"	" = 25.37
1.0	"	"	"	0.2534	"	" = 25.34
1.0	"	"	"	0.2536	"	" = 25.36
1.0	"	"	"	0.2535	"	" = 25.35

Fifty determinations, it is seen, were made in six days. At the end of the sixth day the tension had fallen to 1.85 volts; the accumulators were therefore fully charged by a 10-ampere current, receiving an addition of 54 ampere-hours. Since the total capacity of such an accumulator is over 250 ampere-hours, it is safe to assume that 60 to 70 determinations may be made from one charge; and the experience of years confirms this assumption.

To ascertain whether accumulators in use still retain electric energy, their tension may be measured, or the specific gravity of the sulphuric acid in the accumulator may be determined, as this is higher when the accumulator is charged.

Still another advantage in the use of accumulators is found in the fine quality of the precipitated metal, resulting from the constancy of the current, which much exceeds that from a primary battery or a dynamo. In the Aachen laboratory four pairs of accumulators have been constantly in use since 1888, without need of repair. Four accumulators are used in the analytical laboratory, for which they have proved entirely sufficient, and four in the author's private laboratory.

GENERAL RULES FOR THE HANDLING OF ACCUMULATORS.

The accumulators which are employed for the purpose of quantitative analysis are not shipped from the factory ready mounted for use, as in the case of the smaller types of batteries, but the glass jars, cathode and anode plates, and the acid are packed separately. After the glass jars have been carefully cleaned, the plates are set in and the jars are filled with pure dilute acid (sp. g. 1.15), so that the plates are completely covered by the liquid. The density of the acid is not so important as its purity. Either absolutely pure (chlorine-free) acid must be obtained direct from the manufactory, or

must be prepared by passing hydrogen sulphide gas for several minutes into the "commercially pure" acid. By this operation the traces of metals in solution, which would otherwise prove extremely detrimental to the accumulators, will be precipitated. After the precipitate has subsided and the acid has been decanted, the dissolved hydrogen sulphide is removed by warming the acid for a short time or by blowing in air.

As soon as the accumulators have been set up they are ready for charging. This is done from a suitable source of current according to the number of accumulators at hand.

The charging current should under no circumstances be allowed to exceed the one given for the particular model by the manufactory. It must therefore always be controlled by measuring instruments. The current from a dynamo or thermopile may be most practically used for charging, but in case of necessity Bunsen or the so-called "gravity batteries" may be employed. The peroxide plates are connected with the positive, the lead plates with the negative pole, of the charging current.

If a number of accumulators are to be charged, they are connected in series; the charging current must therefore have an electromotive force proportional to the number of accumulators.

The so-called "capacity" of the accumulator determines the period required for charging. By this is understood its production in ampere-hours. For example, an accumulator of 100 ampere-hours capacity, with a maximum rate of discharge of 10 amperes, may be discharged at a rate of

	10	amp.	for	10	hours,	
or	5	"	"	20	"	,
or	1	"	"	100	"	, etc.*

* Anleitung zu elektrochemischen Versuchen von Dr. Felix Oettel, 1894.

The period of charge is therefore given by the current strength of the charging current when the capacity is known. As already stated, accumulators are reversible elements, and therefore the same number of ampere-hours must be expended in charging them as they themselves are able to furnish when fully charged. The termination of the charging must be determined either by a measurement of the tension, since every accumulator when fully charged has a tension of about 2.2 volts, or the appearance of the formation of gas (so-called "boiling" of the acid) may be taken as the point for stopping the primary current. The appearance of hydrogen shows that the gas is no longer used up to reduce the lead sulphate at the negative pole, and that the reaction upon which the action of the accumulator depends is completed.

When the batteries are charged for the first time it is found best to continue the supercharging (generation of gas) for one hour or over.

On discharging, the tension of each accumulator falls rapidly to 2 volts and there remains constant. As soon as the tension falls below 2 volts the batteries must be recharged.

The manner and method of connecting up the batteries on charging depends upon the nature of the source of current. If a dynamo is at disposal, the accumulators are so coupled in series that the tension of the dynamo exceeds by a small amount the opposed tension of the accumulators (2 volts each). If the electromotive force of the primary current is too high, then it must be reduced, either by introducing resistance or by the employment of a transformer.

If a Gülcher thermopile having a tension of 4 volts is used for charging the batteries, the cells must be differently connected. They are then arranged in parallel, i.e., the similar poles are connected with one another, so that the whole system acts like a single accumulator with a tension of

2 volts. Owing to the small number of amperes furnished by a thermopile, a considerable time is required for charging (8 cells of 8 ampere-hours' capacity each require 32 hours).

To insure the durability of the accumulators, the following rules must be observed: *

1. They must be protected from short circuit.

2. The maximum rate of discharge given by the manufacturers must not be exceeded.

3. Each element must not be discharged below 1.85 volts.

4. The elements must not be allowed to stand in an uncharged condition; also when not in use they must be charged once every 3 or 4 months.

5. Violent shaking must be avoided, since it is apt to cause the falling out of the active material.

[The Electric Storage Battery Co. of Philadelphia, Pa., manufacture a number of types of accumulators which are particularly suited for electrolytic work. Fig. 32 shows a cell of the so-called type E, a form of cell especially suited for small storage plants. The plates are provided with very long lugs which allow the connections to be made at such distance from the acid that the possibility of corrosion is entirely removed. The plates themselves are prepared by the so-called "chloride process," which gives to them great durability. In employing this type of battery in the laboratory, it is best to seal the jars with paraffine. This is done by pouring melted paraffine over the acid in the jar. A good-sized rubber stopper is held with its lower end just touching the surface of the acid, and the melted paraffine is allowed to flow around it. When the paraffine has completely solidified, the stopper is withdrawn or may be allowed to remain loosely in the orifice.

* Cf. Anleitung zu elektrochemischen Versuchen von Dr. Felix Oettel, 1894.

Spattering and evaporation are thus prevented and the cell may be moved about without danger of slopping.

The same Company also make a portable cell (Fig. 33). The accumulators are put up in sealed rubber jars, enclosed

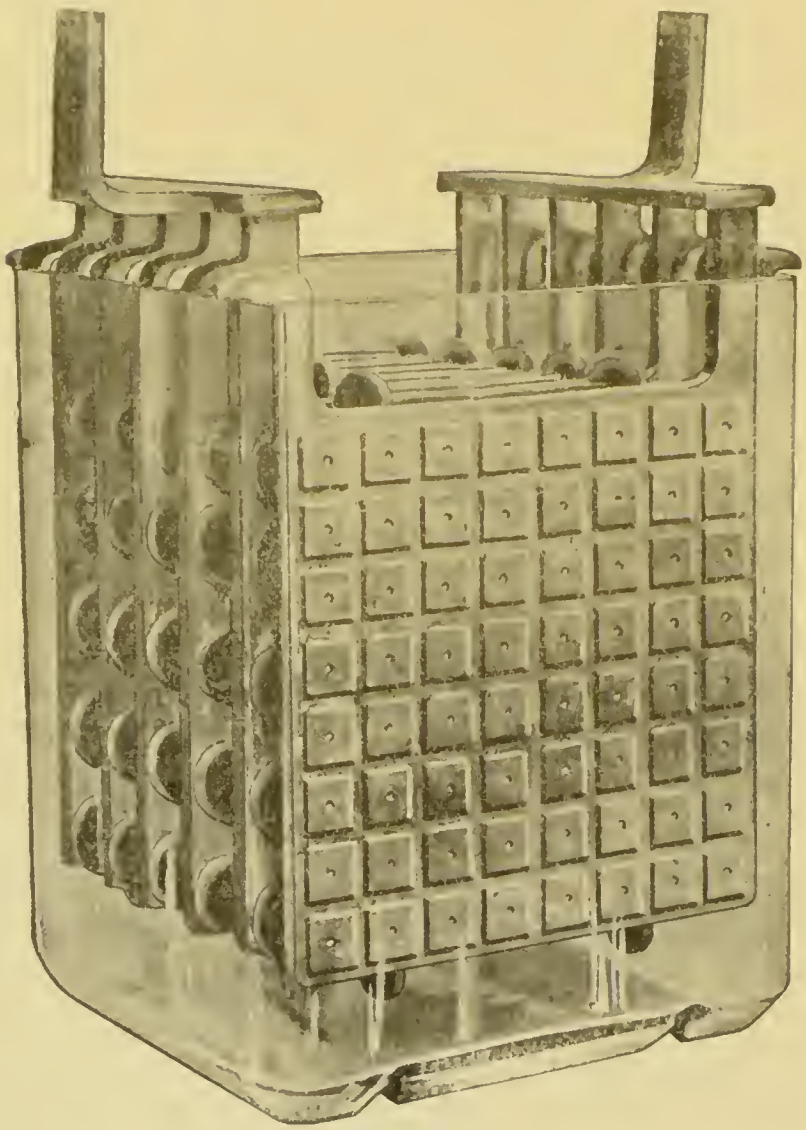

FIG. 32.

in neat hard-wood cases provided with handles and binding-posts. Various capacities are furnished. These cells are especially convenient for small laboratories or others which possess no plant suitable for charging. In such cases the

portable accumulators may be charged outside of the building at some power station at a reasonable figure. With four such

FIG. 33.

cells of, say, 100 ampere-hours capacity each, and the simple arrangement described on page 108, any of the analyses described in this book may be carried out.

The translators are indebted to the Electric Storage Battery Company for their kindness in furnishing the illustrations here given.

The translators have omitted some 20 pages of the German text, devoted to an elaborate argument to prove that secondary batteries are superior to primary galvanic cells as a proximate source of electricity for electrochemical analysis. They consider that fact as fully established in the minds of all who are likely to make use of their work.

It may be as well to say a few words in this connection as

to the source of current. Granted that the secondary battery is the best proximate source, the question remains as to the charging of these batteries. In the great majority of cases, arrangements can be made for using a current that is maintained for other purposes, either sending out the cells to be charged, or charging in the laboratory, using resistances or transformer, according to suggestions elsewhere in this work. Where recourse must be had to a source contained within the laboratory, it may be possible, in technical laboratories, to have a small dynamo run by a belt from shafting belonging to the factory.

In case no dynamo current is at hand, either primary batteries or a thermopile may be employed. A chemist in so isolated a location could either prepare a sufficient number of Daniell cells of the "gravity" type, perhaps making large-sized cells by using pails of moulded fiber, now universally sold, as containers, or could with little trouble and expense construct a thermopile of the Paget type that he would find sufficient for his needs.—*Trans.*]

PHYSICAL METHODS OF PRODUCING THE CURRENT.

ELECTROMAGNETIC MACHINES.

For electrochemical processes, uniform continuous currents of great quantity (low intensity) are required.

The author used for electrolytic analysis, during the years 1881–5, a magneto-electric machine made by Siemens & Halske of Berlin.

A pulley was fixed on the axis of this machine, and connected to a second pulley on a counter-shaft. The counter-shaft carried a cone pulley with 5 steps of 30, 25, 20, 15, and 10 cm. diameter, corresponding to a similar cone pulley on a second counter-shaft. This second counter-shaft was provided with fixed and loose pulleys, and was directly connected with

the source of power. The change of connection of the cone pulleys, therefore, changed the velocity of revolution of the magneto-electric machine.

The observed velocities of the machine, with this arrangement, were 700, 500, 300, 200, and 100 revolutions per minute.

To control still more closely the strength of the current, a regulator was inserted provided with resistance-spirals and 6 contacts, giving resistances of 0.01, 0.02, 0.06, 0.6, 1.45, and 3 ohms; thus the machine was made available for all determinations and separations.

This arrangement is adapted, as will be seen, to carry on simultaneously only similar determinations; it is not possible, e.g., to determine together iron and antimony or copper.

The firm of Siemens & Halske has constructed, for the laboratory of the author, an apparatus which allows a large number of the most unlike determinations to be carried on together without interference. The action of the apparatus depends essentially on an arrangement by which the full current of the machine is sent through an artificial resistance with many subdivisions, and the tension of these subdivisions is kept constant; that is, each subdivision has a constant known tension, which remains unchanged, if a side current of comparatively little strength is taken to carry on a determination.

Before describing the details of the apparatus, it must be premised that the current is produced by a dynamo machine of the form shown in Fig. 25. This machine, at 1,000 revolutions per minute, furnishes a current of 60 ampères with a tension of 10 volts; it requires to run it something more than one-horse power.

Siemens & Halske describe the action of the dynamo as follows: A current is produced in a closed electric con-

ductor when a portion of it is passed between opposite poles, which may be developed in fixed or in moving masses of iron. The direction of this current depends on the position of the magnetic poles with reference to the direction of the motion. The conductor, by the motion of which the electric current is produced, is insulated copper wire wound in several divi-

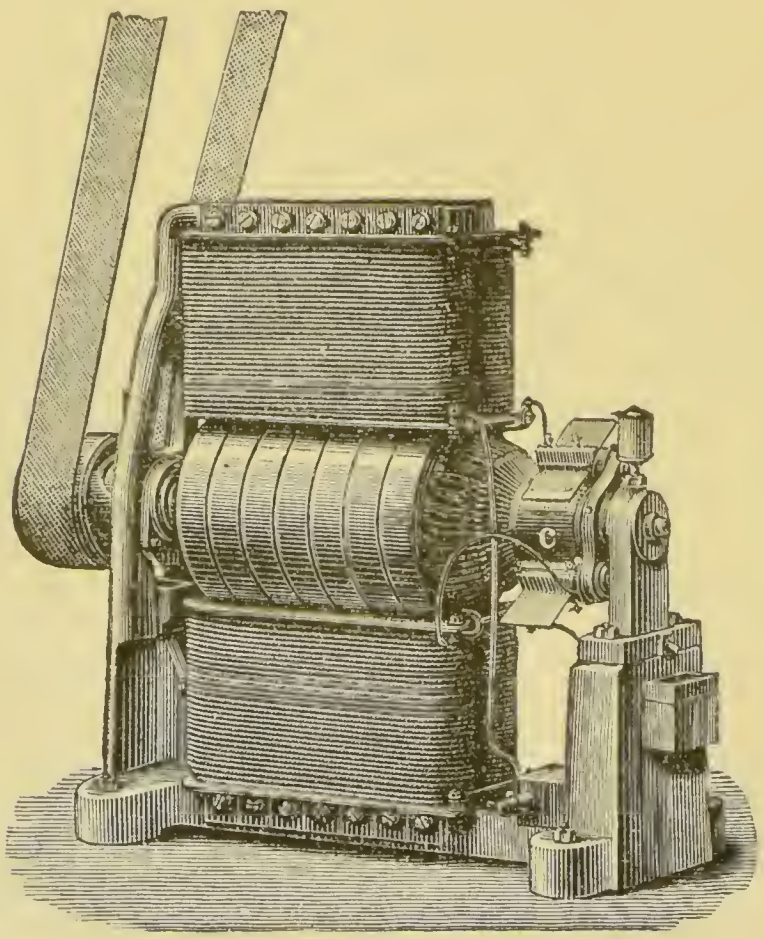

Fig. 34.

sions of many turns each about an iron core, so as to cover it completely, even on the faces. This core is a hollow cylinder of soft iron wires or plates, which revolves on an axis passing longitudinally through it (Fig. 35, *nn'*, *ss'*). Partly surrounding this hollow cylinder on either side, and conforming to it in shape, are iron bars, NN', SS', the straight project-

ing portions of which are wound with insulated copper wire, and connected by the bars *m* and O, thus forming horseshoe electro-magnets, N*m*S and N′OS′, with their similar poles opposite to each other.

By the action of the electro-magnets, powerful opposite magnetic poles are formed in the iron bars to the right and left of the rotating wire-covering of the core.

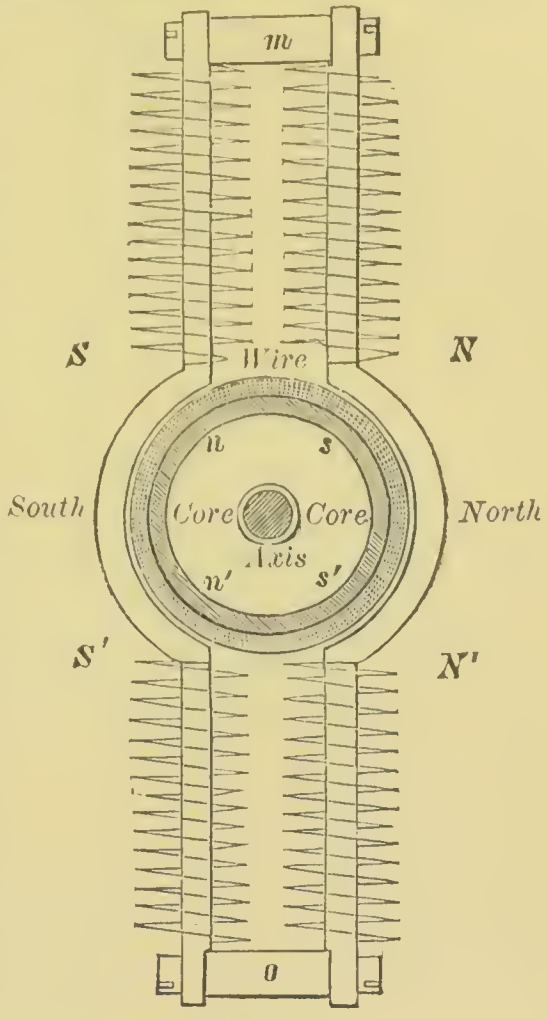

Fig. 35.

The iron core becomes, by induction, a transverse magnet always opposing its poles to those of the outer electro-magnets. The intermediate spaces, in which revolves the wire cylinder covering the core, become magnetic fields of great intensity. Every revolution of the wire cylinder produces in each turn of the wire, as it passes through the two magnetic fields, two currents in opposite directions. By means of a commutator which is connected in a peculiar manner with the single coils, a continuous current (constant in one direction) is produced from the combined action of these single alternating currents. The commutator C (Fig. 34) consists of a number of insulated copper plates, which, taken together, form a cylinder surrounding the axis of the iron core and revolving with it. Brushes of copper wire transmit the current from the commutator to the wire that forms the circuit.

According to the fundamental principle of the dynamo, the electric current which is produced is itself utilized for strengthening the magnetism which is necessary to the machine, the weak magnetism remaining in the iron being sufficient to begin the action when the machine is started. The current, to this end, traverses the wires which are wound about the electro-magnets, as well as the external circuit in which it is utilized.

THERMO-ELECTRIC PILES.

The principle upon which the construction of this form of apparatus is based, is that at the points where two metals are soldered together a difference of potential arises, if the junctions are maintained at different temperatures. Of the various forms of thermo-electric piles which have been brought before the public, those of Clamond, Noë and Gülcher have found practical application.

Clamond's pile (shown in Figs. 36 and 37) is built up of a large number of elements, each consisting of a bar of an antimony and zinc alloy, and a strip of tinned sheet-iron; the iron strips are fastened to the bars as shown in Fig. 38, thus serving to connect the elements. Both the single elements and the superimposed rings of elements are separated by layers of asbestus.

Binding-screws are attached to the poles of each ring of elements. The current is produced by heating with illuminating gas which burns from a perforated cylinder of clay or porcelain, standing in the middle of the pile (Fig. 39, one-third natural size). This tube-burner is cemented in the cylinder with a mixture of powdered asbestus and water-glass, and can be replaced in case of accidental breakage. To keep the flow of gas constant, and prevent exces-

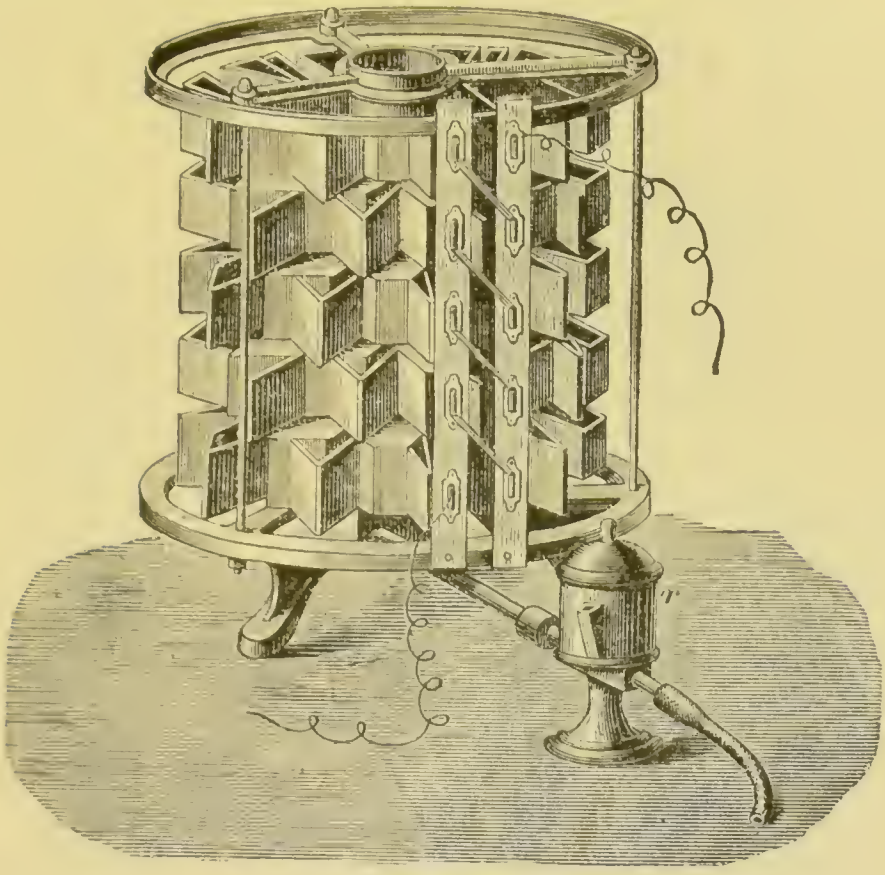

FIG. 36.

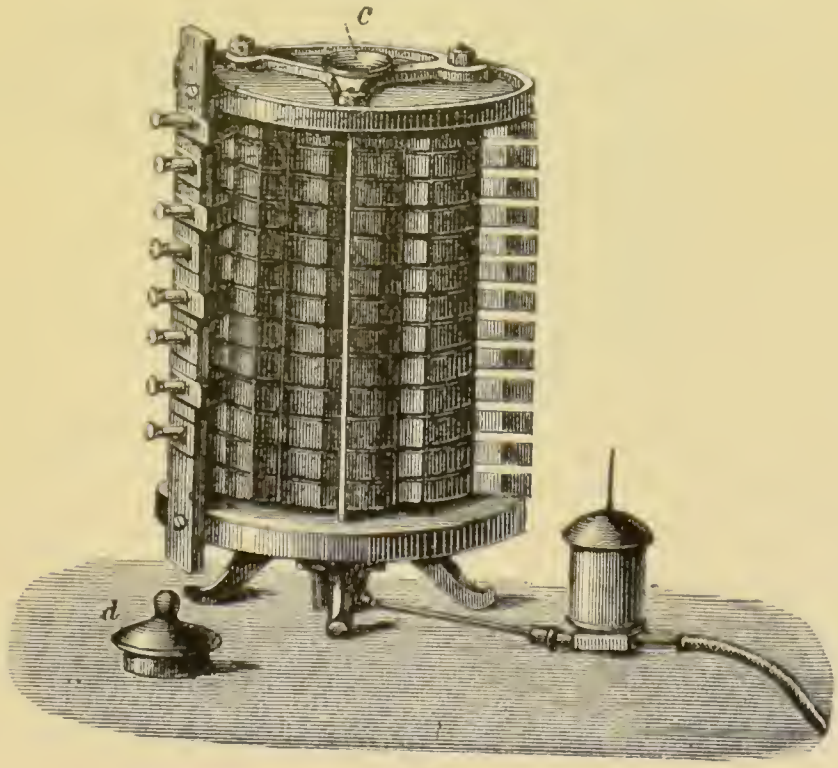

FIG. 37.

sive heating of the burner, the gas is first passed through a regulator filled with water (*r*, Fig. 36), the valve of which partly closes the orifice when the pressure rises, and opens it wider when the pressure falls. The water in the regu-

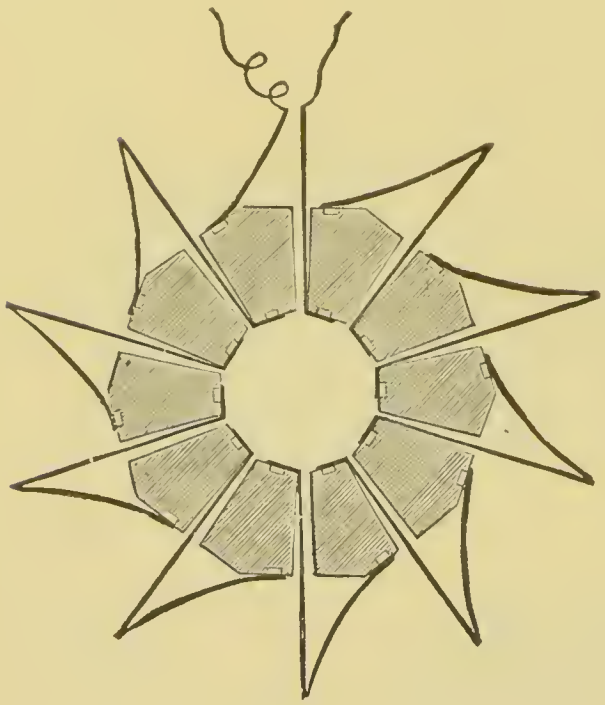

Fig. 38.

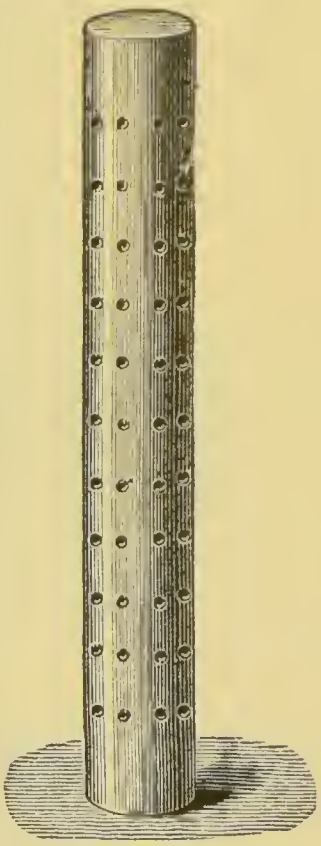

Fig. 39.

lator must be replaced as it evaporates. The current attains its full strength when the gas has been burning about one hour.

After using the pile, care must be taken not to cool the tube-burner too quickly. To this end, the cylinder opening at C (Fig. 37) is first closed with an iron plate *d*; after that the cock is closed.

The elements of Noë's thermopile are rods of an alloy containing 63 per cent antimony and 37 per cent zinc, about 7

mm. in diameter and 27 mm. long (Fig. 40), to each of which

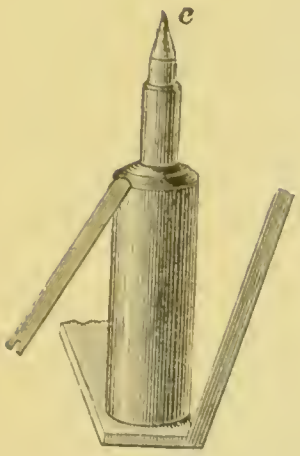

Fig. 40.

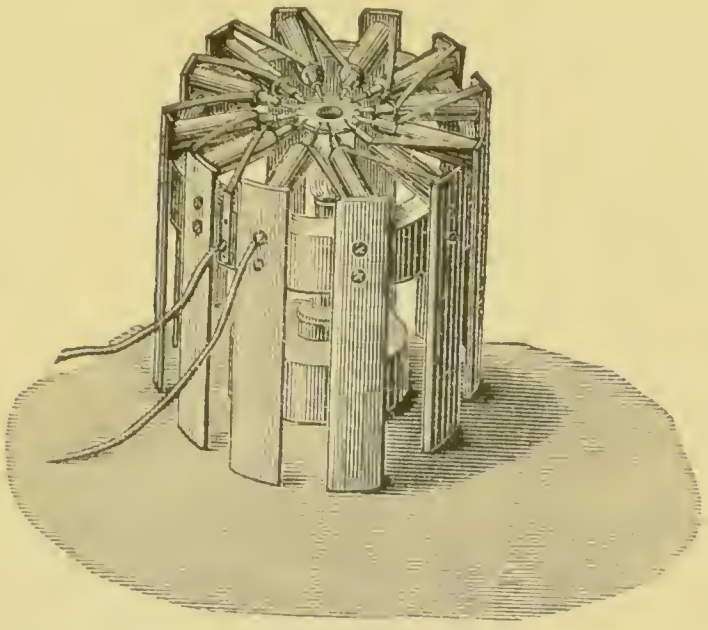

Fig. 41.

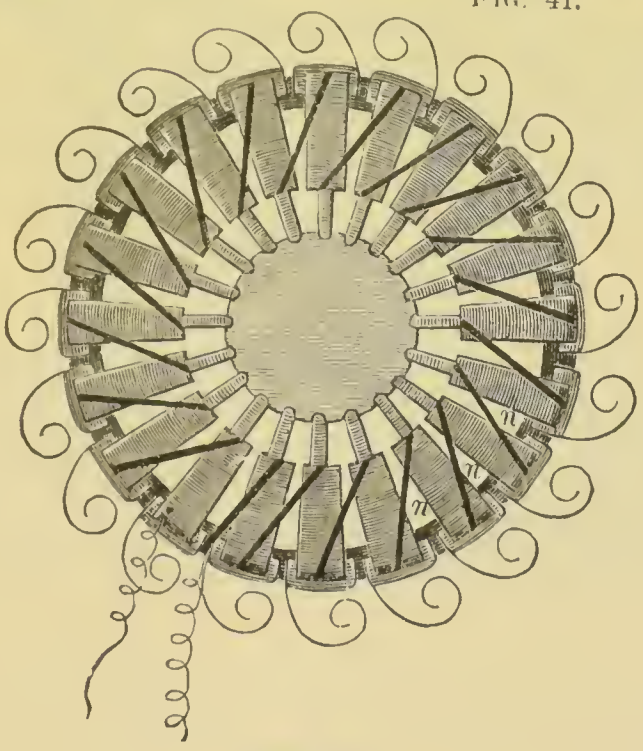

Fig. 42

is attached a smaller pointed iron rod (*e*) to conduct the heat

to it. The elements are arranged in a circle, on a ring of ebonite, with the iron point resting on a plate which serves to spread the flame of the gas-burner (Fig. 41). The connection of the elements by German-silver strips, *nn*, etc., is shown in Fig. 42. The elements are soldered to copper plates set in a circle, which are bent in spiral form, and serve to support the elements, and also to cool their outer ends. Fig. 43 gives a general view of the Noë thermopile. If it is only moderately heated, the air cools it sufficiently; if more strongly heated, it must be placed in a vessel of water.

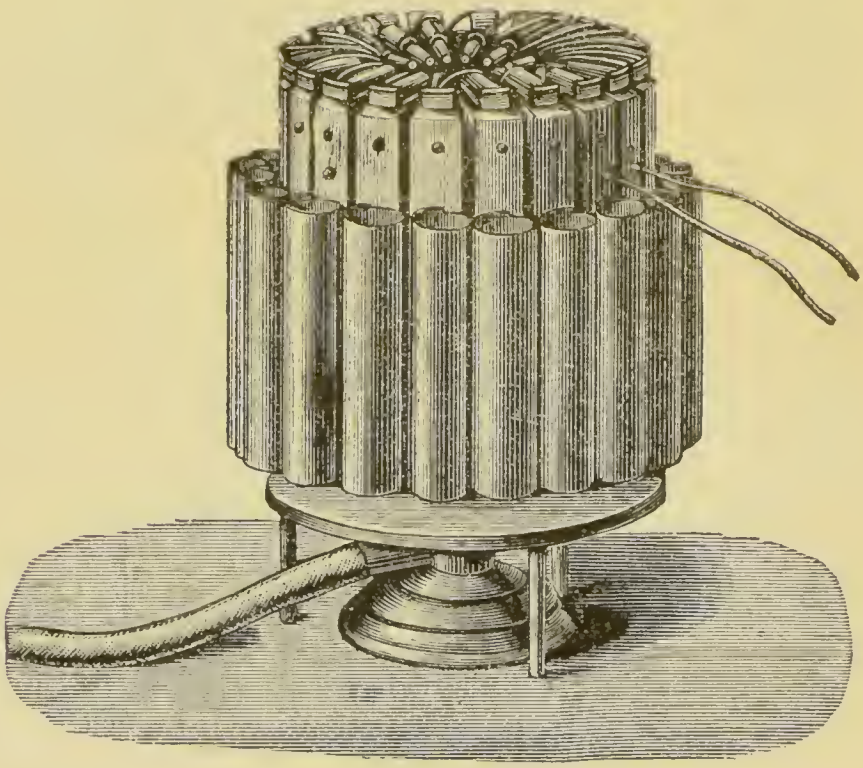

Fig. 43.

According to v. Waltenhofen, a pile of 128 elements in 4 groups of 32 each is equal in electromotive force to about 2 Daniell cells.

Recently a thermopile of new construction, devised by

Gülcher, has proved especially adapted to the requirements of electrolysis. Along the upper side of the pipe which conducts the gas, and which extends lengthwise through the apparatus, are situated two rows of nickel tubes having at the tops small openings which permit the escape of the gas. On the upper ends of the nickel tubes, where the flames are ignited, are soldered plates of an antimony alloy, from which copper strips extend to the bottom of the adjoining nickel tubes, so that considerable differences of temperature exist between the top of one tube and the bottom of the next.

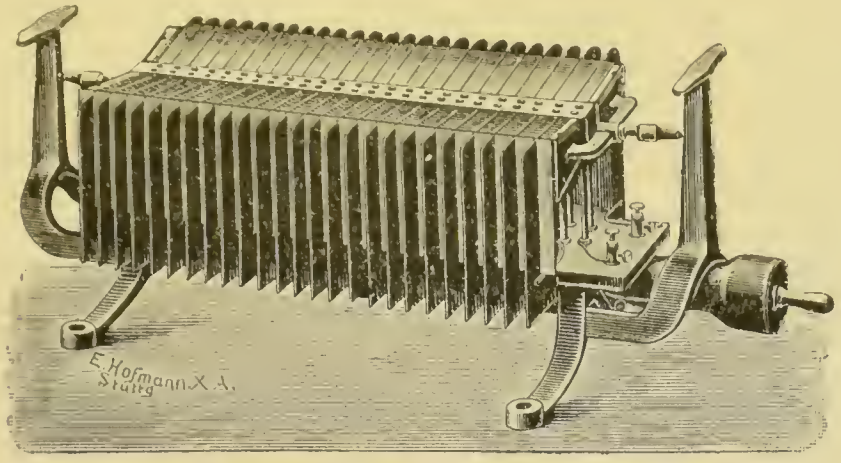

FIG. 44.

Fig. 44 shows an apparatus of the model constructed by the firm of Julius Pintsch (Leipzig). This thermopile, consuming 170 liters of gas per hour, furnishes an electromotive force of 4 volts and has an internal resistance of 0.6–0.7 ohm, so that it may be used for charging accumulators.

Wing-like plates of sheet metal are attached to each of the nickel tubes, and from these fractional parts of the entire tension of the apparatus may be taken off.

The constancy of the tension of the thermopile depends upon the uniformity of the gas-pressure, which in cities is often liable to great fluctuations. Such a condition of

things may often be extremely deceptive, as in the case, for example, where an experiment is continued unobserved throughout the night. Of the many regulators which have been devised to prevent these variations in the gas-pressure, that constructed by Danneel (Göttingen) excels all others in simplicity of construction and operation, as well as in precision.*

The arrangement of the apparatus is readily seen from the adjacent sketch (Fig. 45). The solenoid S receives its current directly from the thermopile, or, if desired, from the pole-clamps of the bath. It fits exactly over the glass tube which encloses the apparatus, and draws downward the magnet M on an increase of the tension. The opposing force is furnished by a spring so arranged that it will not be too greatly stretched by the weight of the core, and still may respond to slight attraction. The spring is attached at its upper end to a thread which is connected with an adjusting mechanism plainly shown in the drawing, by which the tension of the spring can be easily increased. On the iron core is hung the plate of the plate valve. The gas flows in through the base B, and out to the thermopile through A. C is an adjustable screw ending in a cone, which is used for closing a second passage for the gas from B to A, so far that the current of gas passing through is just sufficient to keep the lights of the thermopile from being extinguished when the valve is completely closed. The thermopile is provided with an attachment for regulating the air-supply, in order to prevent the snapping back of the flames when the gas-supply is low. The apparatus is mounted on a

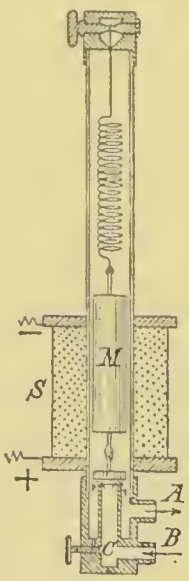

FIG. 45.

* Ztschr. f. Elektrochemie, 1896–97, p. 81.

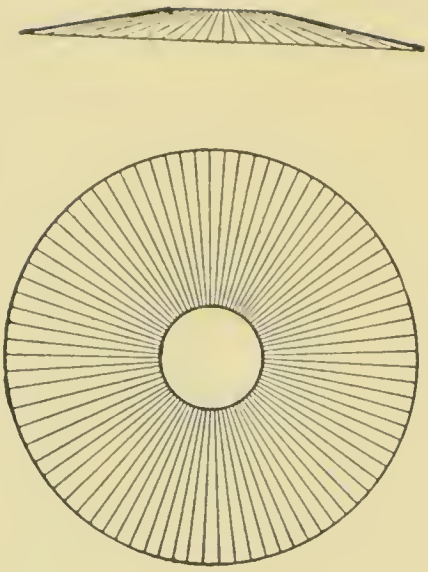

FIG. 46.

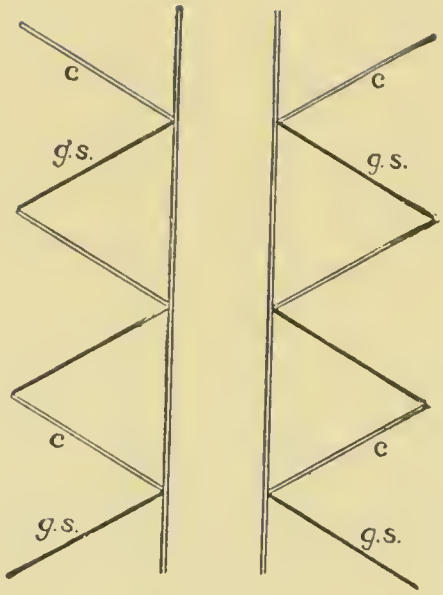

FIG. 47.

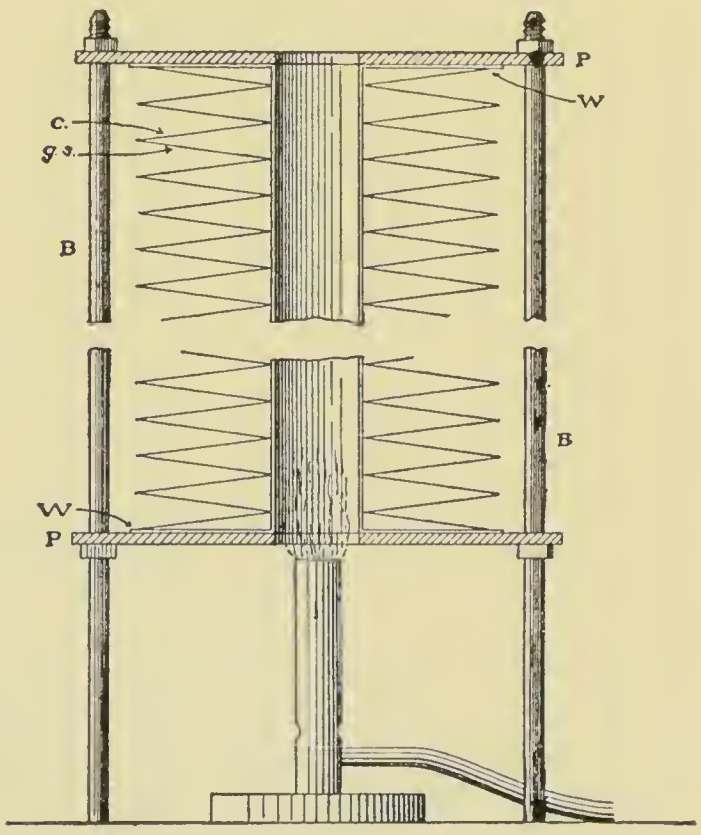

FIG. 48.

To face page 71.

base provided with adjusting-screws. On this is a regulating resistance which allows any desired tension to be taken off direct from the apparatus. The thermopile, which in contrast to most other sources of current can stand short-circuiting, is short-circuited through a variable resistance of coiled wire, and by the adjustment of a curved lever connected with this the desired tension is obtained. Varying the tension in this manner is far more convenient than the usual method of attaching clamps to the vanes of the separate thermo-elements.

The Gülcher thermopile, in combination with accumulators, appears to be particularly suited to the requirements of small electrolytic experiments. An especially convenient arrangement of this sort is described by K. Elbs.*

[Another thermopile worthy of mention is that invented by Dr. Leonard Paget of New York. Although patented, it has not been made in commercial quantities and put on the market, and any chemist or electrician is free to prepare and use one. The inventor has expressly authorized the translators to make this statement, and will answer any inquiries made through them.

The Paget thermopile is very simple in construction, so that it can be made by or under the direction of any chemist or electrician, wherever the services of an ordinary blacksmith or similar metal-worker are to be procured.

It consists of thin annular disks of copper and German silver, buckled or dished (Fig. 46), and placed alternately, one above the other, upon the gas-tube *g* (Fig. 47), so that adjacent disks are held in contact by their own elasticity.† The whole system is held between annular iron plates *pp* (Fig. 48) with

* Chem. Ztg., 1893, pp. 66 and 97.

† The gas-tube *g* in this small pile is conveniently made of asbestus sheet, shaped into tube form about a stick of the desired diameter.

asbestus washers *ww*, by three long bolts *b*; these bolts are prolonged to serve as legs. Heat is supplied by a Bunsen burner. The disks are some 3 or 4 inches in diameter, with an opening 1 inch in diameter.

This thermopile can be taken apart at any time by removing three nuts, and the contact edges of the disks brightened by sand-papering. This will be found desirable after several weeks' use, and can be done in an hour by unskilled labor.

A larger form, used with great success in copper determinations at the Chicago Copper Refining Works, consisted of disks 8 or more inches in diameter, with a 3-inch opening, and was heated by charcoal, the gas-tube *g* being furnished with a simple grate and extended upward to produce a draught. This latter form has been used in the works referred to, in preference to an available side current from a dynamo.

Fig. 49 shows a still larger form, heated by coke on the base-burning principle, which was constructed and used in 1892.

The fire-box is 1 foot in diameter. The annular copper plates *c* are extended to form cooling plates; all air used in combustion being drawn over them, as indicated by arrows. The cylinder was 2 ft. high, with 8 pairs of elements to the inch, and the output in actual work was 11 volts and 72 amperes.

Various modifications will suggest themselves under special conditions, e.g., the adaptation of the size of the disks to the use of one of the more powerful oil lamps as a source of heat.

The sheet metal used for the disks in the smaller sizes is $\frac{1}{32}$ of an inch in thickness. About 35 pairs of the smaller size described give an E.M.F of 1 volt, so that to charge two secondary cells would require about 200 pairs.

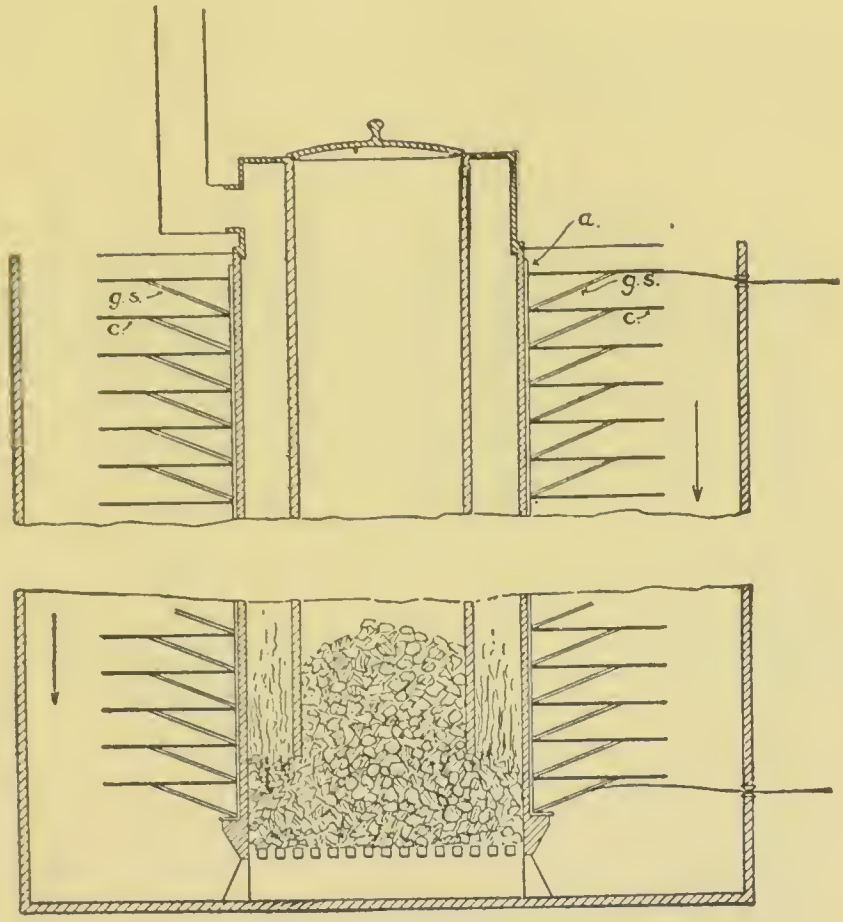

FIG. 49

REGULATION OF THE CURRENT.

The relation of the current strength to the resistance is explained by Ohm's Law; from which it follows that it is never possible to alter either one of the two quantities independently of the other. Variation of the current strength as well as of the tension, as has been previously explained, is of the greatest importance for quantitative electrolysis, and the means at hand for the accomplishment of this are numerous.

When accumulators or primary elements are employed, the tension may be varied by connecting a greater or less

number of them in series. If one element has a tension of a volts, then n elements in series give na volts.

In the case of dynamos, the number of revolutions of the

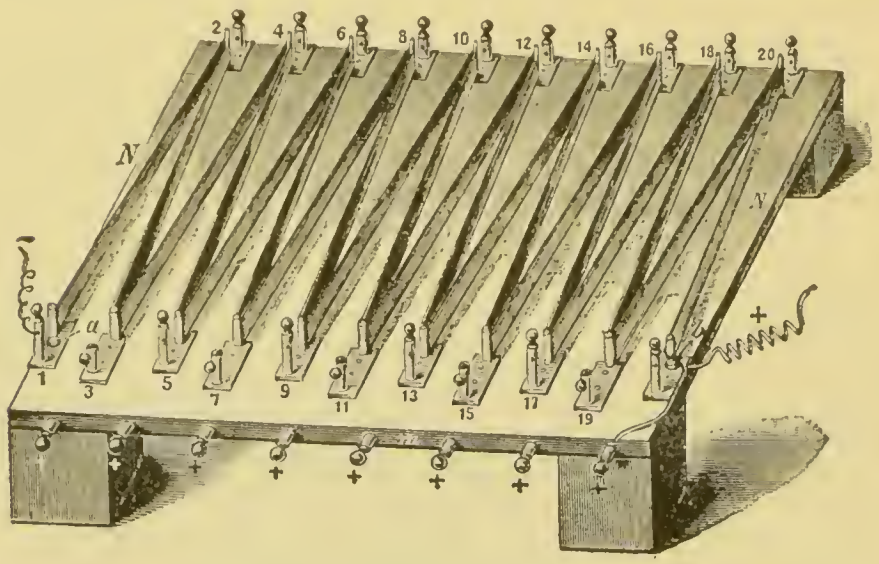

FIG. 50.

armature, as well as the number of windings of the magnet, has a great influence, so that by an alteration of either of these the most varied tensions can be obtained.

A convenient method of altering the tension, which is applicable to every source of current, is the introduction of a shunt circuit, or the use of resistance in the main circuit.

The theory of the shunt circuit is based upon the following considerations: Suppose that the positive and negative poles of a source of current are connected by a wire 100 meters in length, and that the electromotive force is 10 volts. Then along the 100 meters of wire a fall in tension of 10 volts will take place, which will be proportional to the resistance of the connecting wire. If the wire is of equal cross-section throughout and of uniform material, the resistance and correspondingly the fall in tension will be proportional to the length. The fall in tension for every ten meters will there-

fore be 1 volt, for every 1 meter 0.1 volt, etc. If a branch circuit be now attached to two points about 20 meters apart this will have an electromotive force of about 2 volts, and in this manner any desired tension within the limit of the source of current can be obtained. Of course at the same time a corresponding change in the current strength takes place according to Ohm's Law, but since the current strength, at a given tension in the branch circuit, depends upon the resistance of the electrolytic cell, this latter is variable, and with it the current strength with the given tension.

The simple apparatus described in the following has been constructed by the author for this purpose. A plan of it appears in Fig. 50.

The current from the battery enters at *a*, circulates through the German-silver resistance N, and returns to the battery through *b*. In making electrolytic determinations the platinum dishes serving as negative electrodes may be attached to any one of the binding-screws 1–20, while the platinum foils serving as positive electrodes are attached to the binding-screws marked with the + sign. The apparatus, therefore, is suited to carry on eight different determinations simultaneously. Its value for analytical purposes is shown by the following experiments. To determine directly the current strength at the binding-screws 1–20, 150 cc of a 15% copper sulphate solution was placed in each of 6 platinum dishes of equal size, copper anodes* were used, and the current was passed for 7 minutes in each case.

The current was produced by a battery of 5 Bunsen cells.

As already stated, the current strength in the shunt circuit is proportional to the tension, if the resistance remains

* 6 cm. in diameter, 2 mm. thick. The diameter of the platinum dishes was 9 cm., the distance of the electrodes from each other 2.5 cm.

constant. This fact permits of accurate determination of the changes in the tension from the measured variations of the current strength.

First Experiment.

		g. Cu.	Amperes.
Binding-screw	1	0.5064	= 3.75
"	2	0.3507	= 2.617
"	3	0.2873	= 2.085
"	4	0.2358	= 1.711
"	5	0.1857	= 1.348
"	6	0.1453	= 1.054
"	7	0.1341	= 0.973
"	8	0.1128	= 0.818

Second Experiment.

		g. Cu.	Amperes.
Binding-screw	7	0.2213	= 1.606
"	8	0.1622	= 1.177
"	9	0.1356	= 0.984
"	10	0.1083	= 0.786
"	11	0.0846	= 0.614
"	12	0.0744	= 0.576
"	13	0.0506	= 0.367
"	14	0.0410	= 0.225

Third Experiment.

	g. Cu.	Amperes.
Binding-screw 13	0.1983	= 1.446
" 14	0.1304	= 0.946
" 15	0.1276	= 0.926
" 16	0.0855	= 0.620
" 17	0.0605	= 0.439
" 18	0.0385	= 0.280
" 19	0.0314	= 0.227
" 20	0.0136	= 0.098

From a number of quantitative determinations, which were made by Nörrenburg with this apparatus, the following are selected: —

Series I.

The apparatus was attached to a battery of 5 Bunsen cells, and eight iron determinations were made simultaneously. The precipitation was complete in 6 hours.

Taken $FeSO_4, (NH_4)_2SO_4.6H_2O$.	Found Fe.		Binding Screw.	cc. OH Gas.
1.2918 g.	0.1846 g.	= 14.30%	2	24.0
1.4360 "	0.2059 "	= 14.33		25.0
1.1926 "	0.1708 "	= 14.32		24.0
1.1964 "	0.1700 "	= 14.30	3	16.8
1.2945 "	0.1851 "	= 14.30		16.6
1.3218 "	0.1892 "	= 14.31		17.2
1.2931 "	0.1854 "	= 14.34	4	13.2
1.3255 "	0.1895 "	= 14.30		13.4

* The measurements given here, taken from earlier experiments conducted with the oxyhydrogen gas voltameter, now entirely abandoned, permit of the recognition of the correct variations of the intensity, since the same instrument was used in all, and in each case but a short time.

At the close of the experiment the battery (without resistance) still yielded 50 cc OH gas.

Series II.

Three nickel and five copper determinations were conducted simultaneously. The current from 5 Bunsen cells yielded 65 cc OH gas.

Taken Nickel Ammon. Sulph.	Found Nickel.	Binding Screw.	cc. OH Gas.
1.2848 g.	0.1963 g. = 15.28%	2	21.5
1.4341 "	0.2201 " = 15.35		24.0
1.2008 "	0.1842 " = 15.34		22.5
Copper Sulphate.	**Copper.**		
1.1531 g.	0.2910 g. = 25.23%	7	2.5
0.9787 "	0.2476 " = 25.30		2.5
1.0092 "	0.2556 " = 25.32		2.5
0.9938 "	0.2515 " = 25.30	8	2.0
1.0088 "	0.2550 " = 25.27		2.0

Series III.

This established the applicability of the process to the simultaneous determination of nickel, antimony, and copper. The number of analyses again was eight. The battery, of 5 Bunsen cells, yielded 65 cc OH gas per minute.

Taken	Found	Binding Screw.	cc. OH Gas.
Nickel Ammonium Sulphate.	Nickel.		
1.3022 g.	15.30%	3	21.0
1.1520 "	15.27		22.0
1.4391 "	15.32		22.0
Antimony Trisulphide.	Antimony.		
0.1609 gm.	71.44%	9	1.0
0.1691 "	71.47		1.0
0.1626 "	71.49		1.0
Copper Sulphate.	Copper.		
0.2527 g.	25.30	7	3.6
0.2550 "	25.30		3.6

The current strength of the battery at the close of the last two series was about half that at the beginning.

These experiments show plainly the practical advantage of this rheostat. To perform eight iron determinations (Series I) simultaneously without this rheostat would require 8 ordinary rheostats and at least 16 cells. For three nickel and five copper determinations would be needed 16 Bunsen cells and 8 rheostats, or 6 cells, 3 rheostats, and 5 Meidinger batteries of 3 or 4 cells each, the latter for the copper determinations. The conditions would be similar with the third series.

[Prof. Edgar F. Smith uses a simple apparatus (Fig. 51), the accompanying figure and description of which he kindly permits the translator to copy:

"The writer has for some time employed a much simpler current-reducer, which has the advantage of cheapness and ready construction to recommend it. It consists of a light wooden parallelogram, about 6 feet in length. Extending from end to end, on both sides, is a light iron wire, measuring

in all about 500 feet. With the binding-posts at *a* and *b*, and a simple clamp, it is possible to throw in almost any resistance that may be required. It answers all practical purposes."—"Electro-chemical Analysis."—*Trans.*]

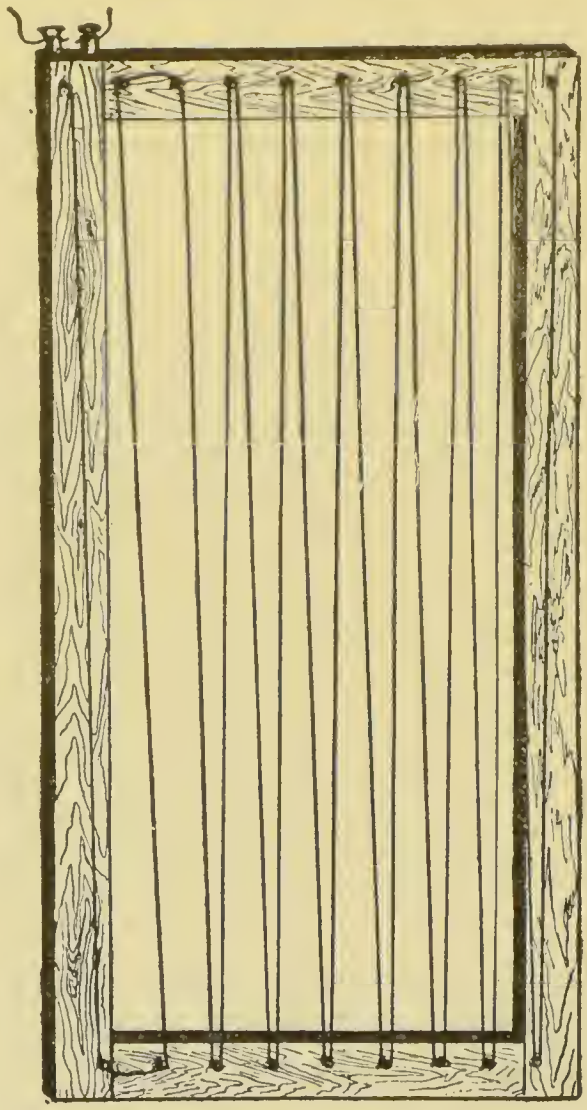

FIG. 51.

A direct alteration of the current strength is in general brought about by the introduction of resistance into the main circuit. It may, however, take place in the elements themselves, whereby several elements are connected in parallel, i.e.,

the similar poles connected with one another. This has the effect of increasing the electrode surface, and consequently decreases the internal resistance.

With dynamos such a parallel coupling is of course not practical.

A much more general method for varying the current strength is through alterations of the external resistance, which can be carried out to a certain extent in the cell itself, by placing the electrodes further apart or by the addition to the solution of substances which increase or decrease its conductivity. Outside of the cell "rheostats" are employed. These are metallic resistances, portions of which may be switched in or out as desired.

Of the innumerable different models, many of which are described in the text-books of physics, only one, of a construction similar to those used for a long time in the Aachen laboratory, will be mentioned.

For the reduction of the current strength, plug rheostats deserve special recommendation. As ordinarily constructed, these are ill adapted to laboratory use, for the plugs are quickly attacked by acid vapors from the cells or the vapors of the laboratory, and the resistance introduced is thus changed. The ordinary apparatus has also the fault that the plugs are liable to become loose. Both difficulties are met by the use of mercury contacts, instead of plugs, to connect the metallic plates. Fig. 52 shows the arrangement of such a rheostat.* By inserting the contact bars CC in the mercury cups or removing them, any resistance from 0.5 to 80 ohms may be inserted by intervals of 0.5 ohms.

The following results of experiment show the action of this rheostat. A current from three Bunsen cells yielding

* This rheostat is made, at the author's suggestion, by Fraas Brothers in Wunsiedel.

in the voltameter 28 cc oxyhydrogen gas per minute was reduced as follows:—

Ohms inserted.	cc Oxyhydrogen Gas per Minute.	Ohms inserted.	cc Oxyhydrogen Gas per Minute.
0.5	16.00	15.0	2.20
1.0	12.50	20.0	1.30
1.5	9.75	30.0	1.10
2.0	7.00	40.0	0.80
3.0	6.00	50.0	0.70
4.0	5.00	60.0	0.60
5.0	4.90	70.0	0.50
7.5	4.00	80.0	0.45
10.0	3.50		

A current of 16 cc oxyhydrogen gas per minute (yielded by two Bunsen cells) was reduced by 40 ohms to 0.4, and by 80 ohms to 0.15 cc oxyhydrogen gas.

More recently the author has used the simplified form of rheostat shown in Fig. 53, in which brass plates are dispensed with, and the contact with the German-silver coils is made directly by mercury.

The following results of experiment show how constant is the current from Bunsen cells when a rheostat is used. In the separation of antimony from tin, the current from two Bunsen cells was reduced to 0.6 and 2 cc oxyhydrogen gas per minute.

Columns A and B give the strength of the two Bunsen elements; columns C and D, that obtained by use of the rheostat.

A and C were measured before the experiments; B and D, after them (lapse of time, 14 hours).

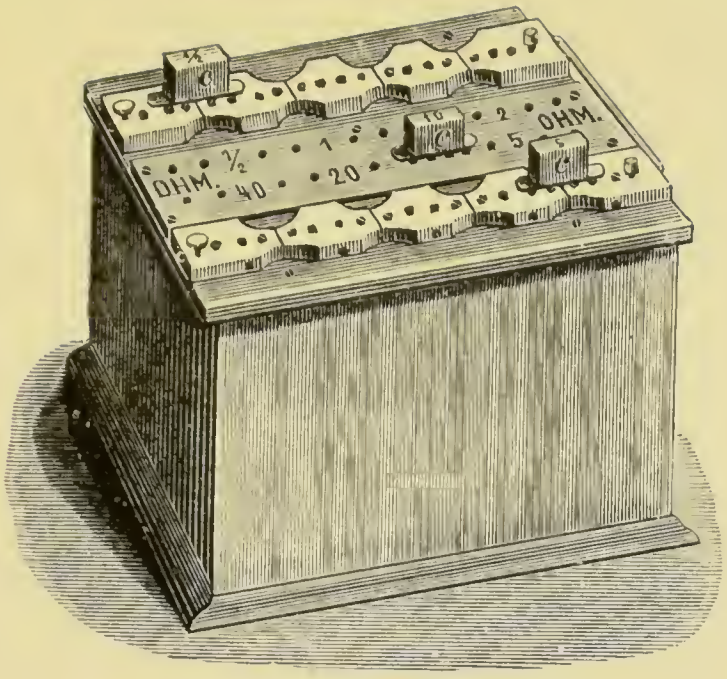

Fig. 52.

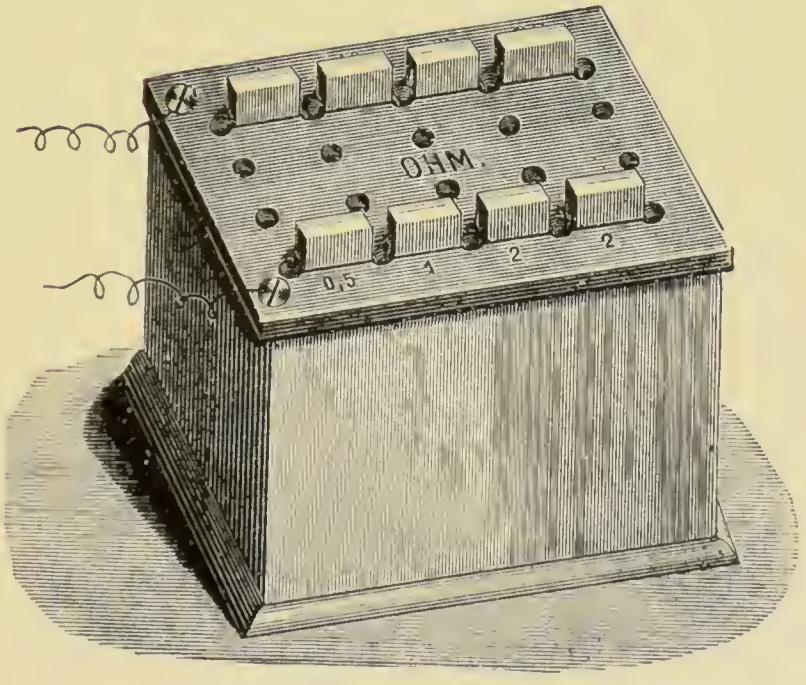

Fig. 53.

To face page 82.

A.	B.	C.	D.
cc OH Gas.	cc OH Gas.	cc OH Gas	cc OH Gas.
17	16.0	0.6	0.3
24	19.0	0.6	0.4
18	11.5	0.6	0.3
17	15.5	0.6	0.4

THE PROCESS OF ANALYSIS.

The performance of a quantitative analysis by electrolysis requires, above all things, *extreme cleanliness*. As it is impossible, in electro-plating, to obtain a metallic coating on any surface which is not most carefully cleaned before it is placed in the bath, so a quantitative analysis cannot be successfully carried out unless the metallic surface serving as cathode is previously perfectly cleaned and freed from fat. The same care must be used with the battery connections, the stand which serves to conduct the current, etc.; otherwise it is impossible to avoid the weakening or breaking of the current.

It is plainly desirable that the surface of the cathode should be large in order that the separated metal may be more firmly attached to it. If a metal separates from a solution in dense form, as is the case in the electrolysis of double oxalates, the possibility of the oxidation of the metal is scarcely increased by enlarging the cathode.

In the separation of peroxides (e.g., lead and manganese peroxides), which are much less firmly attached, the size of the electrode on which they are deposited is of especial importance.

It is not desirable, therefore, to employ a platinum crucible for electrolytic precipitation if more than a few milligrams are to be determined; not only is the surface of the

cathode too small, but the electrodes are not widely enough separated to facilitate the separation of the metal in a dense form.

For these reasons, the author uses as the negative electrode a thin platinum dish of 35–37 grams weight, 9 cm. diameter, 4.2 cm. depth, and about 250 cc capacity. The dish has the form shown, in about one-half natural size, in Fig. 54 Dishes which have become, in the course of time, rough, scratched, or bent, cannot be used for electrolysis.

Some metals separate less readily in hammered dishes than in those which are spun and polished on the lathe.

Fig. 54.

If, for instance, hammered dishes are used for the reduction of zinc from the double oxalate, there always remains, after the solution of the metal in acid, a gray, closely adherent coating of platinum black, which is with difficulty removed even by melted potassium hydrogen sulphate, and which makes further determination of metals in the dish difficult.

For many purposes, as for example the determination of lead in the form of peroxide, the firm adherence of the precipitate to the dish can only be secured by the use of a platinum dish, the inner surface of which has been roughened with a sand-blast.

It is to be recommended that under all circumstances the dishes used for electrolysis be reserved exclusively for their intended purposes.

The great flexibility of pure platinum dishes has been

recently overcome by the use of platinum-iridium dishes. The iridium, of which about 10 per cent is added to the platinum, gives a much greater hardness and resistibility to the utensils made from this alloy than is possessed by pure platinum articles.

As anode (positive electrode), the author uses a plate of moderately thick platinum foil, about 4.5 cm. in diameter,

Fig. 55.

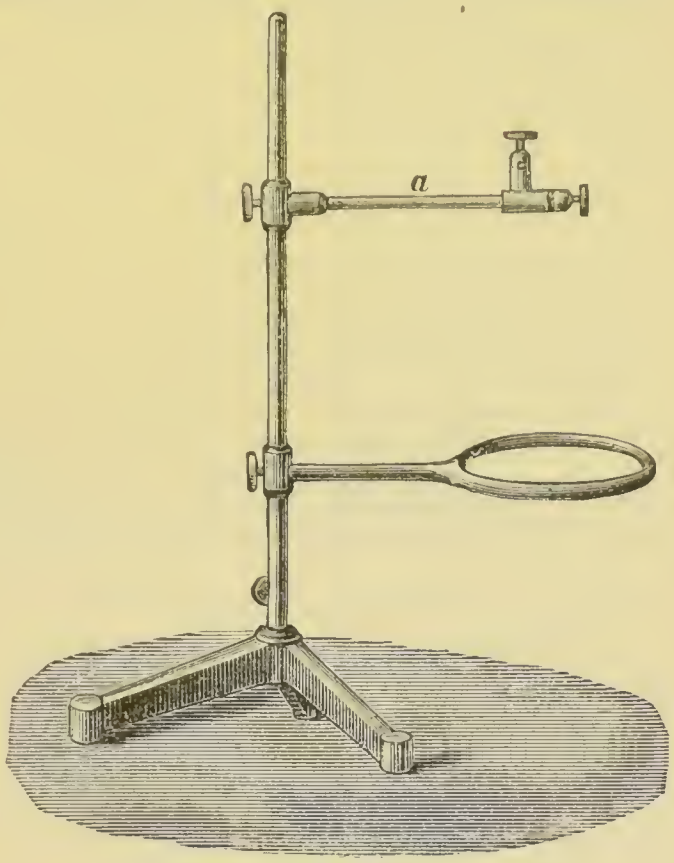

Fig. 56.

which is fastened to a tolerably stout platinum wire (Fig. 55). It is desirable, in order to insure uniformity of the solution during electrolysis, to make a few holes in the platinum foil with a cork-borer. If this is neglected, a large bubble of gas may form under the anode by the union of several smaller ones, and this bubble, on escaping, may cause spirting and loss.

The author has used as positive electrode, in addition to

the one shown in Fig. 55, a platinum dish of the form shown in Fig. 54, 50 mm. in diameter and 20 mm. deep. To secure better circulation of the solution, and more rapid reduction, the electrode has five openings in it. This form of electrode is specially adapted to the determination of such metals as have the tendency to separate in a spongy state, e.g., cadmium and bismuth.

Two standards were formerly used, as shown in Fig. 59, to support the two electrodes. The author substituted a single standard (Fig. 56) provided with a metallic ring to which three short contact wires of platinum are riveted for the platinum dish to stand on, and an insulated arm *a* of glass to support the positive electrode. The use of this stand has the drawback that the brass rod to which the metallic ring and glass arm are clamped is readily corroded by the laboratory vapors, and this may lead to the breaking of contact. The stand shown in Fig. 57 has given good service for a long time. Ring and arm are clamped to a glass rod G, and *n* is connected with the negative and *p* with the positive pole. The positive electrode is clamped in place at *e*. If a platinum cone is used instead of a platinum dish for the deposition of the metal (as described later), two arms are clamped to the glass standard, as shown in Fig. 58. This arrangement is also convenient when a metal is to be precipitated from an acid solution; the standard with the electrodes is removed quickly from the solution and plunged into a vessel of water, and the water is finally removed from the negative electrode by washing with alcohol.

[It is, of course, not necessary to use a special standard constituting a part of the conductor, as shown in the figures. The platinum dish may be placed on the table or the base of a wooden standard, on a coil of platinum or bright copper wire which is connected with the negative pole of the bat-

tery; and the positive electrode may be held in a wooden clamp on such a standard, and connected directly with the wire from the positive pole. See also pp. 89-92.—*Trans.*]

When a platinum dish is used it may be placed on a metal-

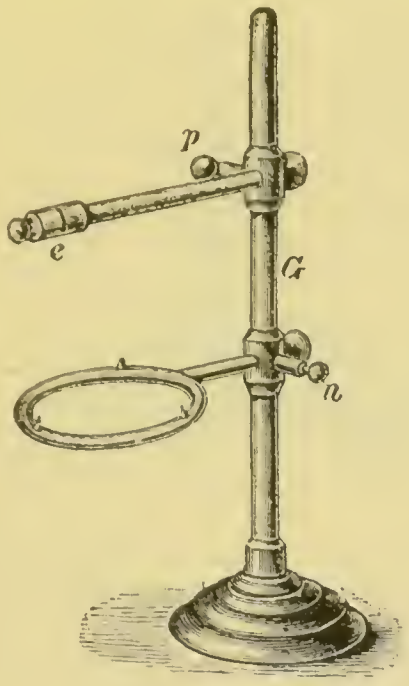

Fig. 57.

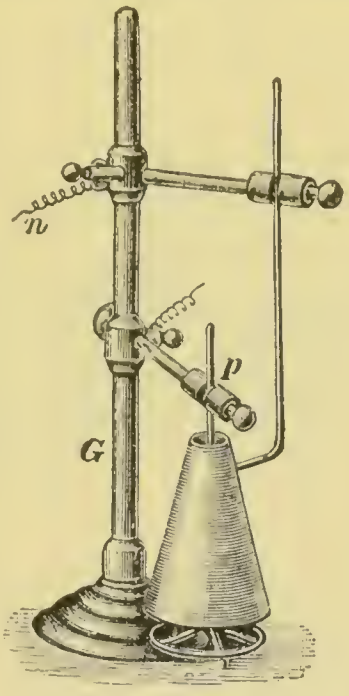

Fig. 58.

lic tripod in a beaker, and the acid displaced by a stream of water from a wash-bottle after the reduction is complete.

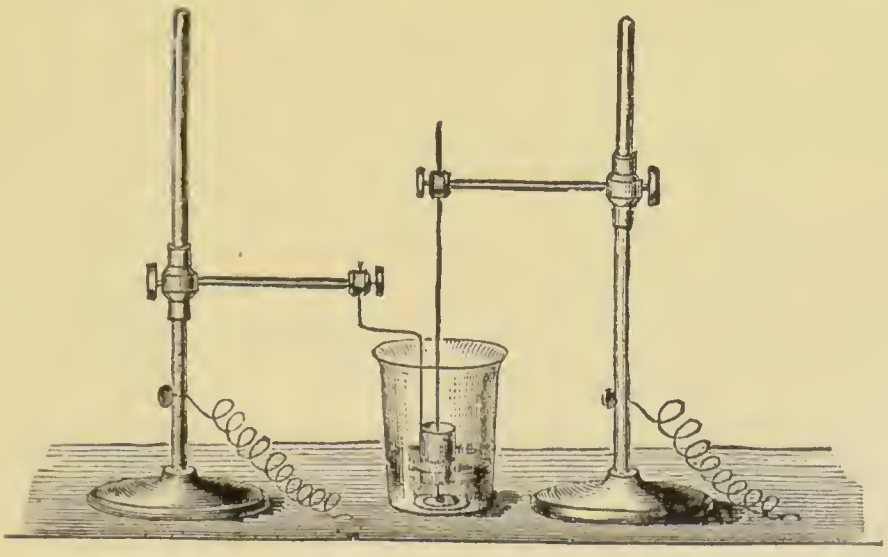

Fig. 59.

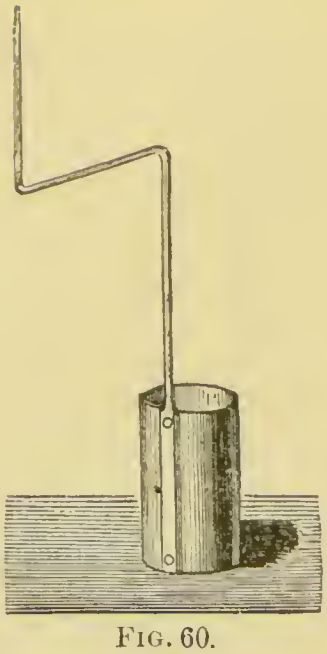

FIG. 60.

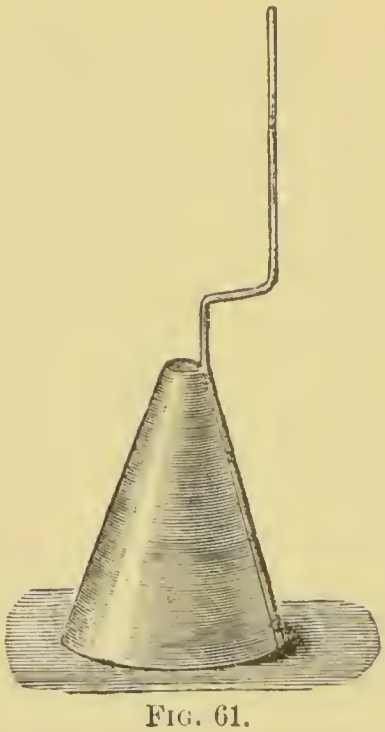

FIG. 61.

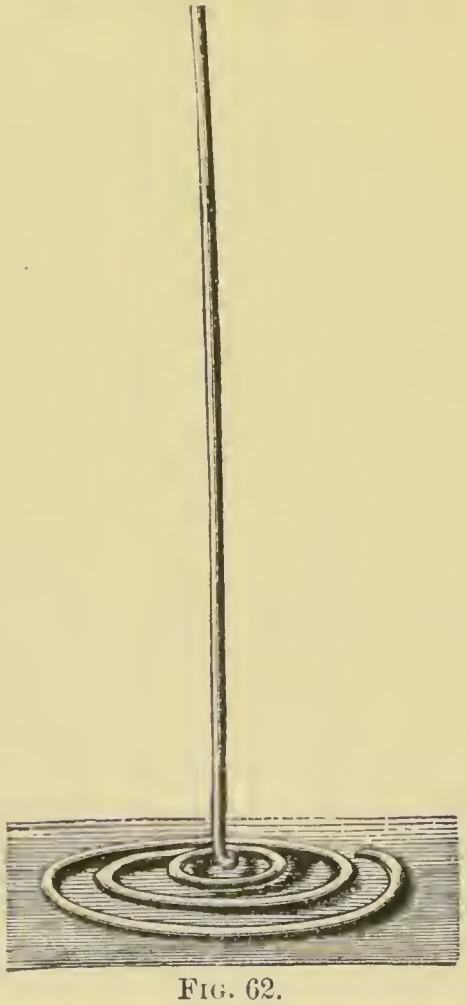

FIG. 62.

FIG. 63.

The electrodes used almost exclusively for copper determinations at the Mansfeld smelting-works are shown in Figs. 59 to 64. According to the quantity of metal to be deter-

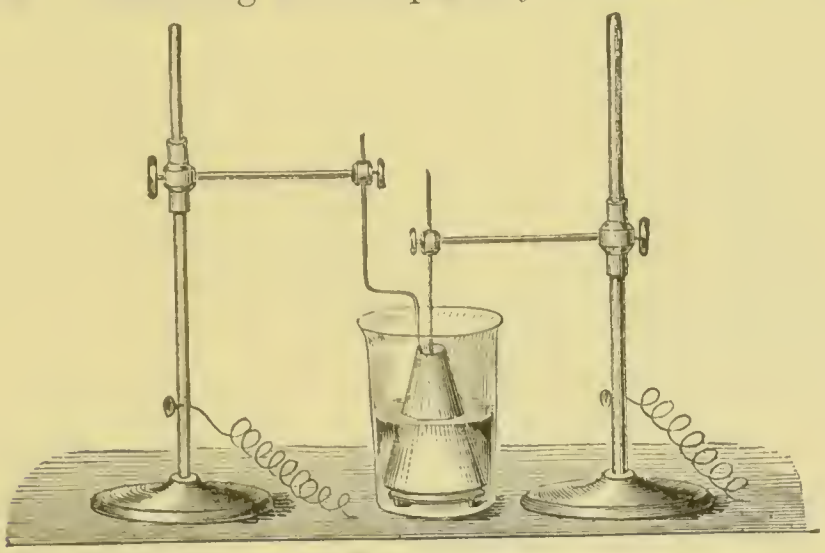

Fig. 64.

mined, the cylinder of platinum foil shown in Fig. 60 (one-half natural size), or the platinum cone shown in Fig. 61 (one-fourth natural size) is used. The positive electrode is either a thick platinum wire wound in spiral form (Fig. 62), or has the form shown in Fig. 63. The arrangement of the several parts is shown in Figs. 59 and 64.

[An apparatus described by v. Malapert* is specially adapted to the use of the above-described electrodes, and particularly to carrying on simultaneously several similar determinations.

As shown in Fig. 65, a single wooden standard A supports the apparatus for several electrolytic determinations, the lower board B carrying the vessels containing the solutions to be electrolyzed, and the upper board C the apparatus for directing the current as desired. In the apparatus described,

* Zts. anal. Ch., 26, 56.

the two boards are 18 cm. apart, and the upper board 7 cm. wide.

Fig. 66 shows, on a larger scale, the arrangement for directing the current, connected with each pair of electrodes. The two strips *bb* of brass are 1 cm. wide, 2 mm. thick, and their centres 3 cm. apart. The binding-screws *aa* serve for the attachment of the elec-

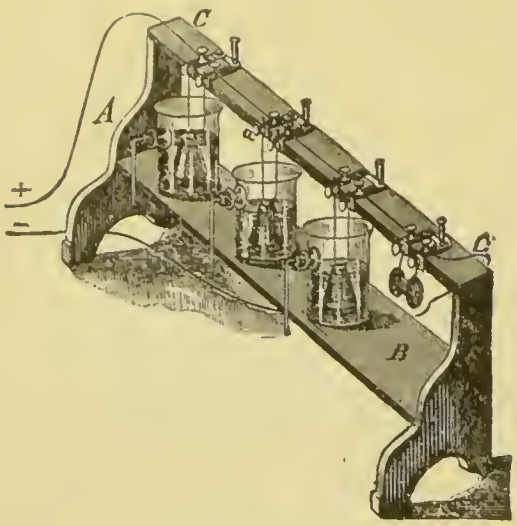

Fig. 65.

Fig. 66.

trodes; to *cc* are attached the conducting-wires. The switch *d* establishes or breaks connection between the two strips according as it is in the position shown in the cut (closed), or is moved to bear on the curved strip of hard rubber *e* (open).

When the apparatus is arranged, as shown in Fig. 65, with the conducting-wires from the battery connected with the end binding-screws, and adjacent binding-screws throughout connected by wires, the current passes unhindered so long as the switches are closed. To insert any desired number of similar solutions for electrolysis, it is only necessary to place the solutions and electrodes in position, and open the corresponding switches; the current is then forced to pass through the solutions.

If dissimilar determinations are to be made, the connecting-wires between adjacent pairs of brass strips are removed, and

the conducting-wires from each battery in use are brought directly to the binding-screws *cc* of one pair of strips.

To remove acid solutions without interrupting the current, v. Malapert uses beakers of heavy glass 8 cm. in diameter and 12 cm. high, with a side tubulure near the top, as shown in Fig. 65. A cork is inserted in the hole between the brass strips shown in Fig. 66, through which passes with little friction a glass tube connected by rubber tubing with a reservoir of water. When the precipitation is complete, a stream of water is turned on, and the acid solution displaced, passing off through the tubulure. A common beaker with siphon can, of course, be used.

A resistance coil of German-silver wire is shown in Fig. 65 connected to the pair of binding-screws at the extreme right. Any desired resistance can be thus conveniently inserted.

An apparatus made according to this description, was prepared for use in the chemical laboratory of the Pennsylvania State College, with an addition, devised by the translator, which makes it equally convenient when a platinum dish is used as the negative electrode.

Fig. 67 shows the nature of the addition referred to. The brass strip connected with the negative electrode is extended downward, at the rear (G, Fig. 67), to the lower board. Here it is connected with the brass plate H, which is set into the board B so as to be flush with its upper surface, and has a shallow saucer-shaped depression, the centre of which is directly beneath the binding-screw to which is attached the positive electrode. The plate H and the entire strip were cut, in the apparatus originally made, from a single sheet of brass.

A platinum dish placed in the saucer-shaped depression is firmly supported, and is in good metallic connection with the

negative pole of the battery; the positive electrode is attached as in the original form of the apparatus. All the adjustments of the original apparatus are retained, and the brass plate offers no impediment to the use of a beaker with cone-shaped negative electrode, as shown in Fig. 65.— *Trans.*]

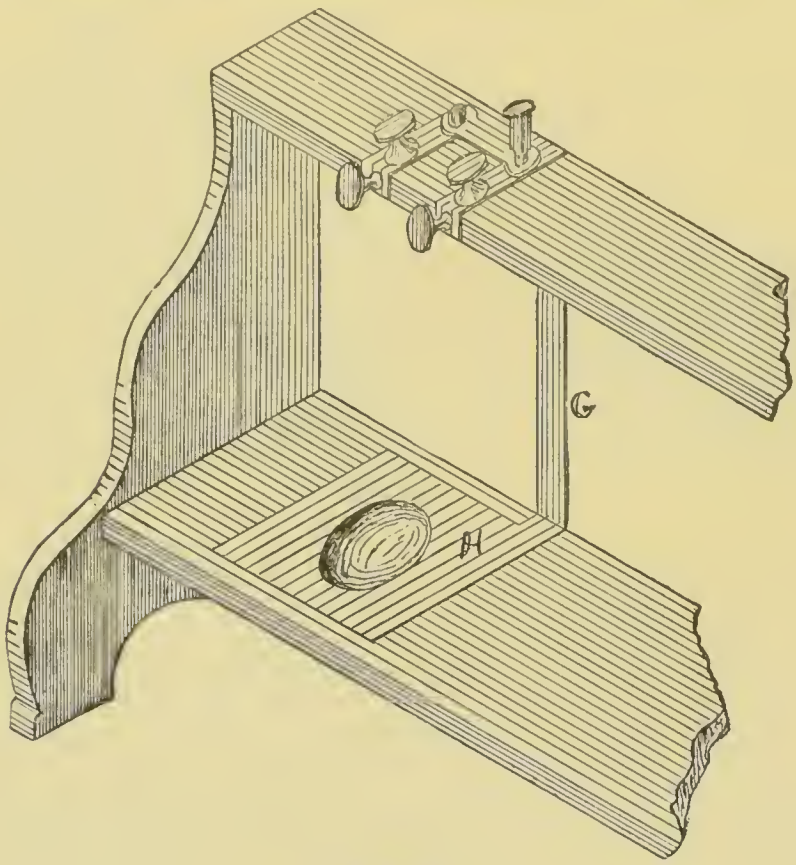

FIG. 67.

Herpin uses, for electrolysis, the apparatus shown in Fig. 68. The platinum dish P standing on the tripod F is connected with the negative pole, the platinum spiral S (shown separately in Fig. 69) with the positive. The dish is covered with a glass funnel T to avoid loss by spirting of the solution.

Riché uses, as cathode, a platinum cone (Fig. 70) open at both ends, having the form of a crucible, and provided

with a bail. Oblong openings are made in the cone to facilitate a uniform concentration of the liquid during reduction. The cone is placed in a platinum crucible so that it is 2 to 4 mm. from it. The whole arrangement is seen in Fig. 71.

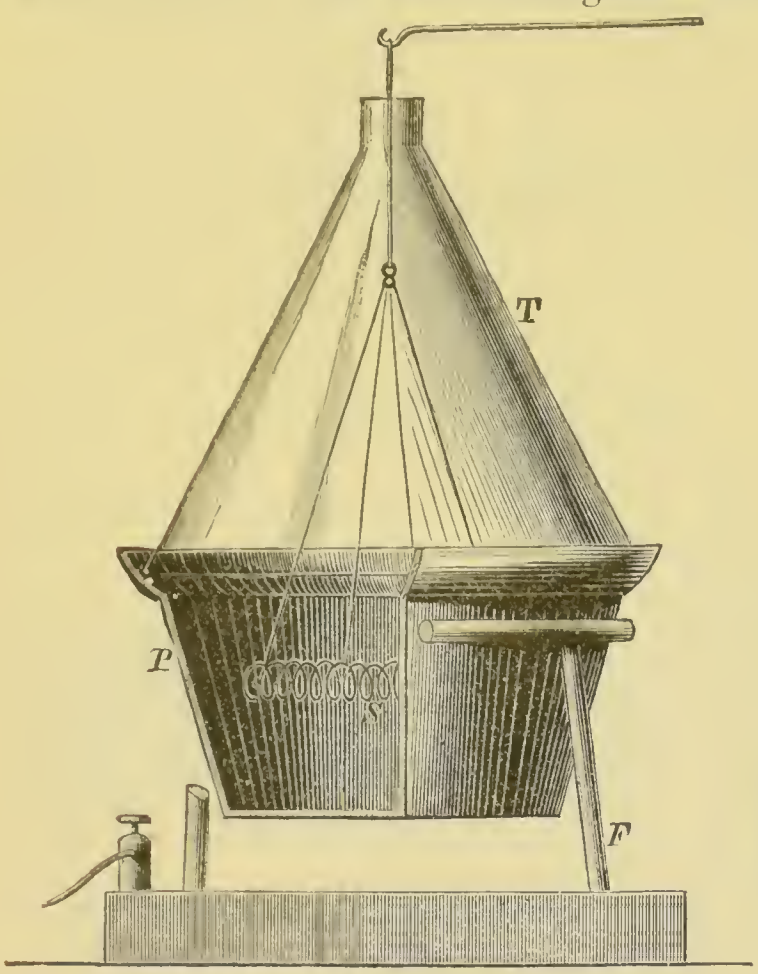

FIG. 68.

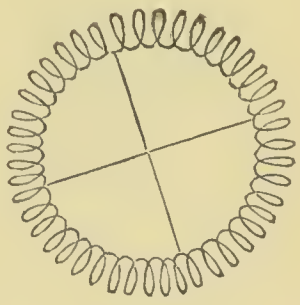

FIG. 69.

To return to the consideration of the actual electrolysis: sulphates are best adapted to conversion into double oxalates (see p. 5), chlorides less so, and nitrates entirely unadapted. If chlorides have been used, and the smell of chlorine is observed during the electrolysis, ammonium oxalate must be gradually added to the solution till the odor

disappears. Sometimes potassium oxalate, sometimes ammo-

FIG. 70.

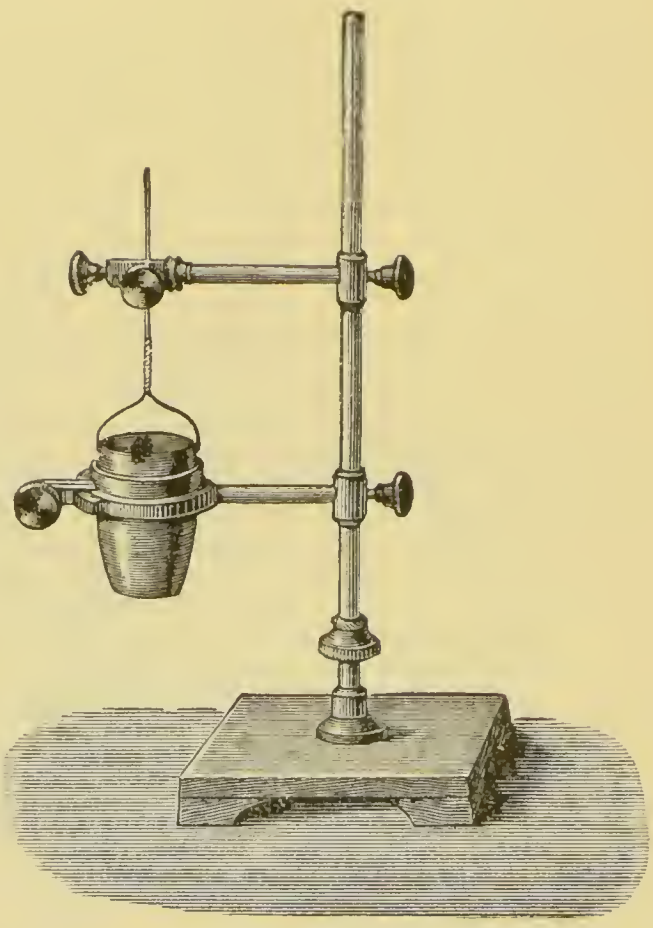

FIG. 71.

nium oxalate, and often a mixture of the two, is used for the preparation of the double salt.

As hot solutions conduct the current more readily, solutions are often heated before they are submitted to electrolysis. In some cases, however, as in the determination of antimony, it is neeessary that the solution should be of the ordinary temperature.

In certain determinations and separations, it is best to keep the solution to be electrolyzed at moderate heat, not above 50°

C. The following experiments show the influence of heat on the time required for electrolysis. Nearly equal weights of iron and nickel were precipitated, under as equal conditions as possible (strength of current, concentration, etc.), from solutions kept respectively at 50° and 15°:— .

Iron.

Taken.		Found.	Strength of Current.	Time.
			cc OH Gas.	h. m.
I. 0.2385 g Fe_2O_3	(Cold) .	0.2384	11	4 20
I. 0.2345 g Fe_2O_3	(Warm),	0.2342	11	2 10
II. 0.2246	(Cold) .	0.2244	10	4 10
II. 0.2369	(Warm),	0.2369	10	2 15

Nickel.

Taken.		Found.	Strength of Current.	Time.
			cc OH Gas.	h. m.
I. 0.2660 g Ni	(Cold) .	0.2660	13	7 25
I. 0.2660 g Ni	(Warm),	0.2659	13	2 20
II. 0.2660 g Ni	(Cold) .	0.2661	13	7 30
II. 0.2660 g Ni	(Warm),	0.2660	13	2 20

It also results from the foregoing experiments, that the current-strength can be greatly reduced by the use of hot solutions, in case there is no occasion for hastening the electrolysis.

The statements in this book apply to solutions at the ordinary temperature, except when the contrary is stated.

For heating the solution to about 50° (it must on no account be heated to boiling, else the reduced metal will flake off from the platinum, and cannot be determined), the burner shown in Fig. 72 is used. The tube of a Bunsen burner may also be unscrewed, and the luminous jet issuing from the opening at the bottom, reduced to a few millimetres in height, used to heat the solution. The distance of the

dish from the burner must be about 15 cm. To insure uniform distribution of the reduced metal on the dish, it must be uniformly heated. This is most simply accomplished by placing under the dish a piece of thin asbestos paper cut through at the points of contact of the dish with the contact wires of the standard. The use of asbestos paper also diminishes the danger of boiling.

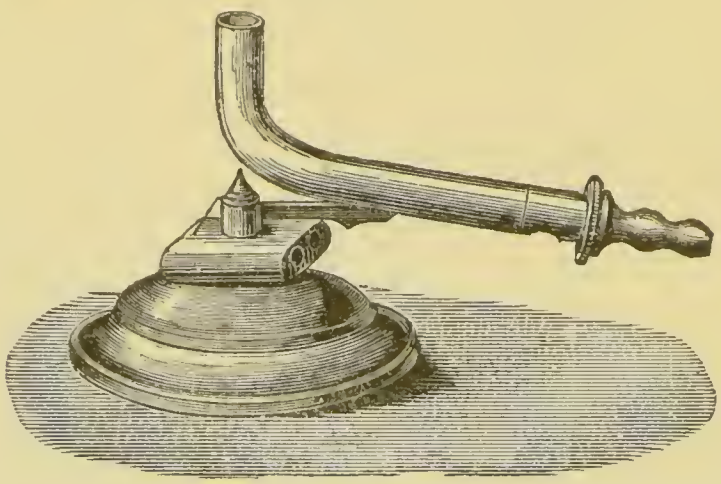

Fig. 72.

In order to obtain a uniform, easily regulated heating, Engels* recommends, as a result of investigations conducted in the Aachen laboratory, the use of an asbestus board at a distance of 2 cm. above which the dish is held by the standard, and under which there is an ordinary Bunsen burner. The dish is thus maintained in an air-bath, the temperature of which can be easily kept constant, and the heating is quite uniform. Such is not the case, however, in the other methods of warming. There, at the points where the dish and stand are in direct contact, a higher temperature arises, and as a result a greater precipitation takes place at these points than on the other portions of the dish.

* Zischr. f. Electrochemie, 1895–96, p. 413.

When the current acts for a long time it is impossible to prevent some evaporation of the solution, whereby a part of the reduced metal is exposed to the action of water-vapor and air. To prevent the oxidation of metal laid bare by evaporation, a little water is poured from time to time on the glass cover of the dish, so that the metal remains always covered by the solution.

After precipitation is complete, the solution remaining in the dish is poured into a beaker, with care to avoid loss, the dish washed three times with about 5 cc of cold water, and then three times with *pure* absolute alcohol. The dish is dried some five minutes in an air-bath at 70°–90° C, allowed to cool thoroughly in a desiccator, and weighed.

The apparatus hitherto described have, without exception, been the result of work conducted in the Aachen laboratory. Other forms of apparatus, which to a limited extent have also found application, have mostly originated from v. Klobukow. He describes a universal stand (Fig. 73) which carries upon a rod screwed into the work-bench all the apparatus necessary for electrolysis.

"If a platinum dish is used as electrode in performing the electrolysis, then the ring *R*, to which three platinum points are soldered, serves as a holder for the dish *s*. The second electrode *E* is clamped into the holder *d*, the latter being adjustably attached by means of the sleeve *D* to the cross-arm *TT*, of hard rubber. The path of the current is as follows: From *m* to the dish *s* by means of the metallic rod, from there to the electrode *E* and thence along *d* to the binding-screw *n* fastened at the end.

"The conducting wires are connected to the rocker W, firmly fastened to the work-bench and coupled into the circuit from the source of current. In addition there are wires attached to the voltmeter, the ends of which may be properly

connected with s and E for the measurement of the potential differences at the electrodes.

"Additional parts of the 'universal stand' are: the micro-burner B, which serves to warm the liquid in s during the electrolysis, and the bottle F, provided with a siphon of special construction, and containing the liquid to be used for

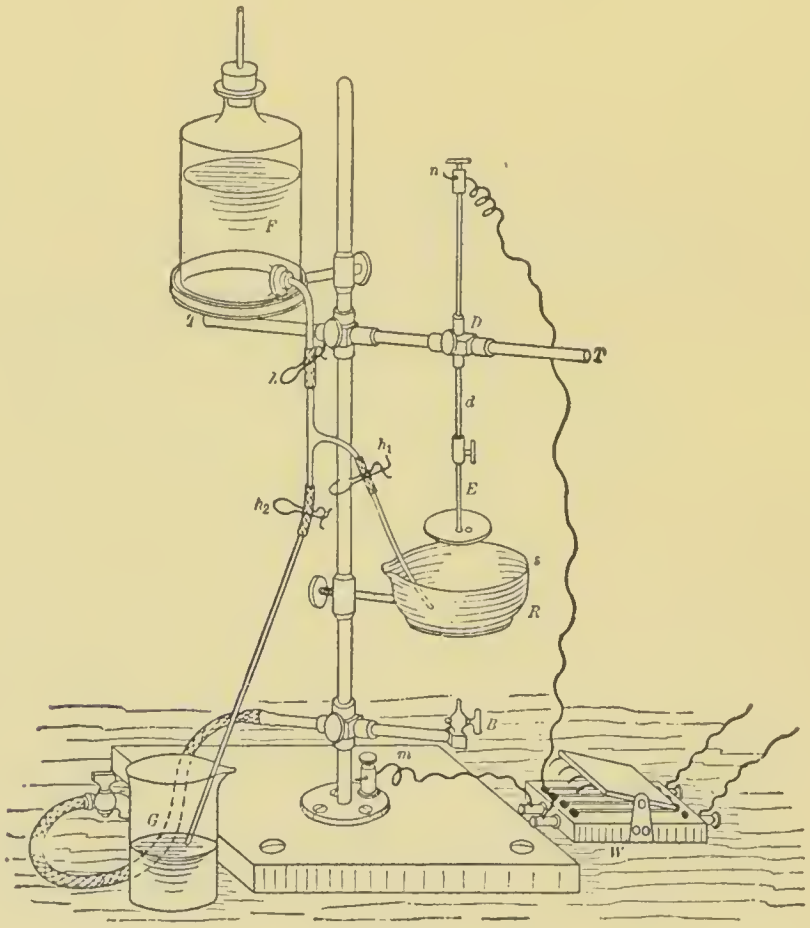

Fig. 73.

washing the metallic precipitate in the dish. The construction of the siphon mentioned is such, that by opening the cocks h, h_1, h_2 in proper order the washing liquid is on the one hand introduced into the dish, and on the other hand the contents of the dish are transferred to the beaker G."

The form of the electrode *E* given by v. Klobukow differs from that described by the author, in that it is convex on its lower surface, the curvature corresponding exactly to that of the bottom of the dish.

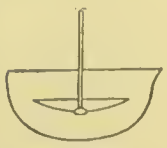

Fig. 74.

This construction is, indeed, in accordance with the theoretical principles, but from the author's experience it is not necessary. It is curious that the metallic precipitates generally have a better appearance when flat, rather than curved, electrodes are employed. (See Fig. 74.)

For his universal apparatus, v. Klobukow proposes at the same time the use of a stirring attachment. With this

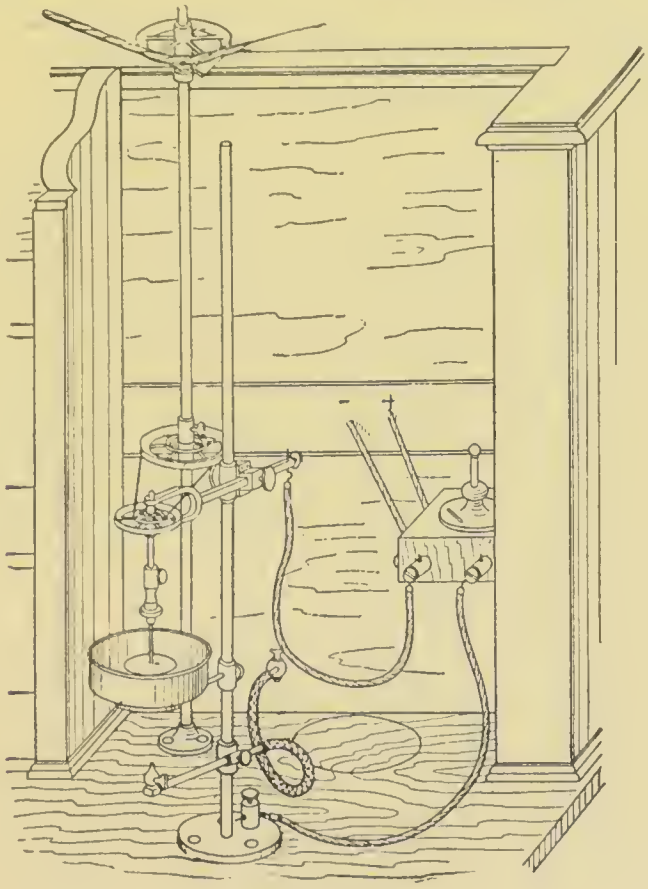

Fig. 75.

a slow rotary motion is given to the electrode *E* by means of a suitable motor connected with it. (See Fig. 75.)

For the special purposes of electrolysis, in addition to the electrodes and dishes described, there have been made a large number of suggestions which are all based more or less upon the same principle. The elbow apparatus, also originated by v. Klobukow, deserves mention. This allows the gases set free at the electrodes to be separately collected, and accordingly permits of a quantitative examination of the same. The apparatus is readily understood from Fig. 76. The corks, which are preferably paraffined, carry thick platinum wires to which the round flat plates which serve as electrodes are welded at angles of 45°. The form of the electrodes is, of course, not confined to any particular one; v. Klobukow also suggests round fluted platinum foils, spirally-wound wire, or pointed electrodes.

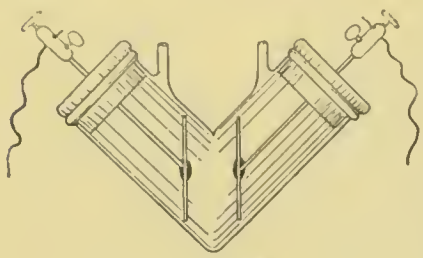

Fig. 76.

In case the anode and cathode liquids are to be kept separate by a porous membrane, v. Klobukow proposes the arrangement shown in Fig. 77. The two separate arms have close-fitting ground faces, which are cemented into a brass mounting. A tight joint is obtained by a hinge and screw.

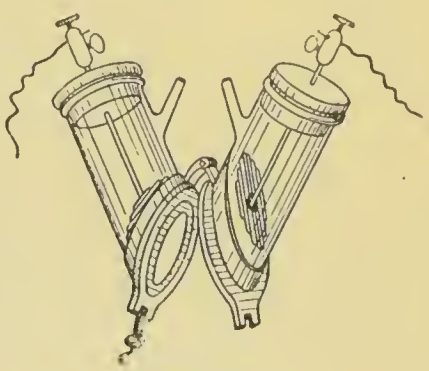

Fig 77.

An electrolytic apparatus, depending upon another principle and serving other purposes, which nevertheless might be useful for quantitative work, is described by Hofer.* Fig. 78 shows two electrode chambers of glass provided with inlet and outlet tubes for the electrolyte, which is con-

* Ber. deutsch. chem. Ges., 27, 461.

ducted in a continuous stream through the apparatus. There is also an escape tube for the gases generated. The two halves, between which parchment paper or other porous diaphragm is interposed, are fastened together by means of a firmly cemented connection provided with a screw. The electrodes have the form of spirals of platinum wire, 0.8 mm. in thickness, or of small platinum plates attached to wires. The connecting wires pass through the gas outlet tubes, and in case the gases are to be collected, they are carried on through T tubes placed at the top and made tight with rubber stoppers.

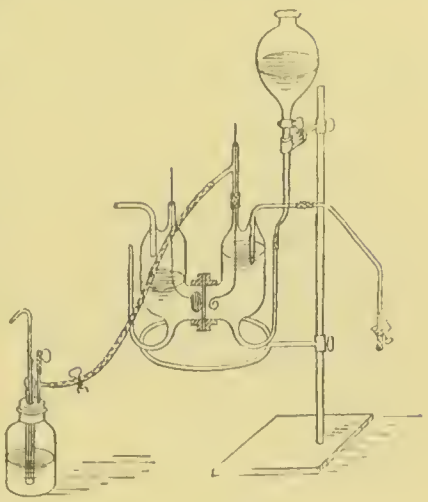

FIG. 78.

The liquid to be electrolyzed is contained in a dropping-funnel, the tube of which is connected by rubber tubing to the lower inlet tube of one section of the apparatus. The liquid is thus continuously brought to the particular electrode and is made to circulate through the cell from the bottom to the top. It flows out through the outlet tube, thence through a piece of rubber tubing provided with a screw pinch-cock for regulating the flow, and into a vessel placed at a lower level.

This piece of apparatus, which has hitherto been used only for the study of organic decompositions, might perhaps be suitable for the quantitative determination of gases.

HISTORICAL.

As in every other new branch of science, the development of electrolysis has been purely empirical. From a great number of observations, collected with diligence and perseverance, in

course of time the most suitable conditions were determined, while the nature of the reactions was not always exactly understood. It was reserved to the most recent development of electro-chemistry to throw light upon the important factors of quantitative electrolysis, and to make clear the signification and value of the current magnitudes and other conditions.

The first researches on the electrolytic determination of metals were of a purely qualitative nature. Shortly after the discovery of the decomposition of water by the electric current, Cruikshank (1801) brought forward the conjecture, based on observations of copper separation, that the galvanic current might be used for the qualitative determination of metals. Very little interest was taken in his suggestion. Fischer (1812) identified arsenic by electrolysis, Cozzi (1840) the presence of metals in general in animal fluids; also Gaultier de Claubry (1850) recommended the employment of the current for discovering poisonous metals in mixtures which contain organic substances.

Charles L. Bloxam (1860) took up Gaultier's researches and worked out many methods which attempted to make possible the identification of arsenic and antimony in the presence of other metals. He was able to rely to a certain extent upon the directions of Morton (1851) for the separation of metals from mixtures.

It had already been observed by Becquerel (1830) that lead and manganese often separated, not as metals at the negative pole, but at the positive pole in the form of oxides, a fact which permitted of the ready separation of these metals from others. A series of investigations on the decomposition of inorganic metallic salts then followed by Despretz (1857), by Nickles (1862), and by Wöhler (1868), of entirely qualitative nature. Likewise the summary of the electro-chemical in-

vestigations of A. C. and E. Becquerel only gave a synopsis of the qualitative electrolytic reduction of the metals.

The results in this direction were accordingly so abundant, that, based upon them, quantitative electrolysis developed with comparative rapidity.

The field of quantitative investigation was first opened by W. Gibbs (1864), who carried out an investigation on the electrolytic determination of copper and nickel, which included a description of the methods for the determination of silver and bismuth in the form of metals, as well as of lead and manganese in the form of peroxides. He also published studies on the separation of zinc, nickel, and cobalt. The possibility of the quantitative determination of copper was confirmed by Luckow (1865), who had worked at it for a number of years. The quantitative electrolytic determination of metals was entitled by him "electro-metal-analysis." This author published at the same time a series of directions for the method of using the current for analytical work, and by these precise instructions laid the foundation for many later researches.

The attention of investigators was now directed principally towards the chemical reactions taking place in the cell with the use of different sources of current and under varying physical conditions. The questions as to the suitable salts of the metals and the appropriate solvents to be used and the proper substances to be added to the solutions were investigated and determined. Wrightson (1876) called attention to the fact that the presence of other metals influences the accuracy of copper determinations, and ascertained the limits for which the presence of antimony in copper still permitted the accurate determination of the latter. The results obtained with cadmium, zinc, and other metals were as yet unsatisfactory.

At the same time as the announcement of the electrolytic determination of gallium in alkaline solutions by Lecoq de Boisbaudran (1877), the first investigation of Parodi and Mascazzini appeared (1877). In the latter, notice was given of the determination of zinc from the solution of its sulphate, to which had been added an excess of ammonium acetate. The authors also found it possible to quantitatively precipitate metallic lead from an alkaline tartaric acid solution containing an alkali acetate.

To Richert (1878) we owe the first accurate directions concerning the determination of manganese. He observed that this metal may be completely separated from solutions of the nitrate in the form of an oxide at the positive pole. This characteristic made possible the electrolytic separation of manganese from other metals, as copper, cobalt, nickel, zinc, etc.

Some of the papers appearing at the same time by Luckow, F. W. Clarke, and J. B. Hannay treat of the electrolytic determination of mercury, which readily separates from solutions of its chlorides or solutions of mercurous sulphate.

F. W. Clarke (1878) succeeded in finding a method for the electrolytic determination of cadmium by separating the metal from solutions of its acetate, a circumstance which Yver (1880) employed for separating cadmium from zinc. Cadmium is not precipitated in the presence of nitric acid, by which the same author succeeded in separating this metal from copper.*

Beilstein and Jawein (1879) satisfactorily employed solutions of the double cyanides in the determination of zinc.

According to Fresenius and Bergmann (1880), nickel and cobalt were successfully separated from solutions which contained an excess of free ammonia and ammonium sulphate.

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* This method, however, is not quantitative.

Smith (1880) started upon the first of his series of investigations with the electrolysis of uranium acetate, which allowed the quantitative separation of the uranium in the form of a hydrated sesquioxide, a property which is shared by molybdenum in solutions of ammonium molybdate containing free ammonia.* Further investigations of this well-known chemist include the electrolysis of salts of tungsten, vanadium, and cerium, and more recently experiments on the separation of metals from potassium cyanide solutions.†

Luckow (1880) rendered special service in the publication of his observations on the reactions which take place during electrolysis in addition to the reduction of the metals. He pointed out the reduction from higher states of oxidation to lower in the case of chromic acid, iron, and uranium salts. He showed, on the other hand, that sulphites and thiosulphates are oxidized to sulphates. Luckow embodied the results of his observations in the law, that in general the action of the electric current on acid solutions is that of reduction, on alkaline solutions that of oxidation.

A. Classen and his students, in the year 1881, began investigations on quantitative analysis by electrolysis, which embraced the observation of nearly all the metals. Classen first pointed out the value of oxalic acid and of the oxalates in the form of double salts with metals (1881).‡ He also

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* According to the investigations undertaken by M. Heidenreich (Ber. deutsch. chem. Gesell., **29**, 1587) this method gives unsatisfactory results.

† Compare experiments given in the special part.

‡ Smith, in his Electrochemical Analysis (p. 44), states that Parodi and Mascazzini (Gazetta chim. it., vol. 8, p. 178), in the year 1879, therefore two years before the appearance of the author's publication, had already announced that iron and antimony could be separated in a dense form, if solutions of the sulpho-salts of antimony and chloride of iron containing acid ammonium oxalate were electrolyzed. The article by Parodi and Mascazzini referred to states as follows: "Questi due metalli si depongono

worked out a large number of electrolytic methods, the details of which will be given under the corresponding metals.

At about the same time Reinhardt and Ihle recommended the oxalic acid double salts for the determination of zinc.

Gibbs attempted (1880), by the use of a mercury cathode, to determine the metals through the increase in weight of the mercury, a method which Luckow (1886) applied also to the analysis of zinc.

Since the year 1886 a great number of publications have annually appeared, the enumeration of which would require too great space.

Nevertheless the experiments of Vortmann (1894) on the electrolytic determination of the halogens by the employment of a silver cathode are worthy of mention. The silver halides adhere firmly to the electrode, the increase in weight of which gives directly the quantity of halogen which has separated.

Greater stress was laid on the physical relations in the investigations which originated exclusively from the observations of Kiliani (1883) on the significance of the tension in electrolytic experiments. Le Blanc was the first to determine the decomposition tension values for solutions of various metals, and through his work laid the foundation based upon which Freudenberg (1891) conducted a separation of several metals by a mere variation of the tension.

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sotto forma elementare compatti e perfettamente aderenti sul polo negativo in platino e cive: l'antimonio dal chloruro diluito nel tartrato ammonico basico ed anche dalle dissoluzioni dei solfosoli; il ferro dal sesquiossido disciolto nel l'ossalato acido di ammoniaca." It is therefore evident that the authors used tartaric acid solutions for antimony. The author (Classen) first proposed the use of ammonium oxalate in the determination of iron. The acid ammonium oxalate employed for this purpose by Parodi and Mascazzini is not at all suited for the determination of iron, since, in the first place, it forms no soluble ferrous double salts, and, in the second place, from solutions of the ferric double salts not even a trace of iron is precipitated until the acid ammonium oxalate has been decomposed by the current.

As the methods of electrolysis were gradually developed, apparatus suitable to the special requirements were constructed. The instruments and arrangements for quantitative electrolysis at present in general use have originated in the Aachen laboratory, where, moreover, both dynamos and accumulators were for the first time employed as sources of current.

ARRANGEMENTS FOR ANALYSIS.

The question as to the most practical equipment for electrolytic research does not permit of a general answer, owing to the many details, such as the construction of the building, the arrangement of rooms, etc., upon which it depends. After solving the problem as to the most serviceable source of current, and deciding in favor of accumulators in combination with a dynamo or thermopile, the details of the equipment can only be described from a certain point of view, according to the requirements which must be fulfilled. The laboratory at Aachen has followed the development of quantitative electrolysis, and beginning with the smallest and simplest equipment has gradually attained a most elaborate one. Three equipments may therefore be profitably described; first, the simplest and most useful arrangement for small requirements; second, the former; and third, the present electrolytic outfit of the Technical High School at Aachen.

Krüger * has published a general review of the equipment of electrolytic laboratories, which contains many valuable suggestions, the repetition of which, however, would occupy too great a space. The choice of special apparatus depends so much upon the individual taste that exact directions are

* Elektrochem. Ztschr., 2, pp. 73, 104, 129, 174, 207, 251; 3, 7, 76, 129.

practically impossible. Indeed Krüger warmly recommends a set of instruments the practical advantages of which have not been confirmed in the Aachen laboratory.

ARRANGEMENT FOR SMALLER EXPERIMENTS.

The equipment needed for carrying out a single electrolytic experiment when a constant source of current is at hand is an extremely simple one.

A standard, with a dish and electrode, and instruments for measuring the tension and current strength, are all that are required. Since, however, it is often desirable to conduct several experiments simultaneously on a small scale, an arrangement will be described which has the advantage that it may be constructed by every one who makes use of electrolysis.

The chief requirement is that it shall be possible to constantly observe the tension and strength of the current. This may be accomplished with the use of one amperemeter and one voltmeter for any number of experiments, in the following manner:

A wooden block, *I* (Fig. 79), is placed before the binding-post to which the negative pole of the source of current is at-

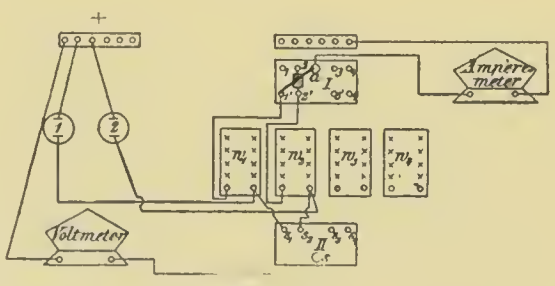


FIG. 79.

tached. This block has a number of holes bored in its upper side, and into these holes are set inverted thimbles filled with

mercury. These mercury-cups are arranged so that there are five in a row along one edge and four along the other. (Fig. 80.)

Fig. 80.

A resistance-box for the regulation of the current is required for each separate experiment. The description will be limited to four simultaneous electrolyses.

The rheostats w_1, w_2, w_3, w_4, of the form designated in the sketch, are then placed in front of the block *I*, and a second block, *II*, having four mercury-cups on one side and one on the other, is added. An amperemeter and a voltmeter complete the outfit.

The connections are made as follows (Fig. 79): Four short wires extend from the negative pole into the mercury-cups 1, 2, 3, 4, of board *I*, the fifth cup of which, *a*, is connected directly with the amperemeter. The second binding-screw of the amperemeter is connected by a wire to the negative pole. Four short wires lead from the corresponding mercury-cups of board *I*, 1′, 2′, 3′, 4′, to the resistance-boxes w_1, w_2, w_3, w_4, the other binding-posts of which are connected both with the electrolytic cells and also with the mercury-cups s_1, s_2, s_3, s_4, of board *II*, in the corresponding manner. The mercury cup *s*, situated by itself on board *II*, opposite the four mercury-cups just mentioned, is connected with the instrument for measuring the tension; and the second binding-post of the latter is connected by a wire to the positive pole. In order to complete the circuit it is only necessary to connect the cups 1–1′, 2–2′, 3–3′, 4–4′ by short bent wires. For the cell 1, for example, beginning at the negative pole, the current pursues the following path: Negative pole, 1–1′, w_1, cell 1, positive pole. The current travels likewise in the other experiments. In order at the same time to measure the current strength, the wire connection is laid from *a* to 1′ (2′,

3′, 4′) and the connection 1–1′ is broken (correspondingly 2–2′, 3–3′, 4–4′). By this arrangement the current, in passing from the negative pole, is forced to flow through the amperemeter, thence over a–1′ to the rheostat, etc. In order that the correct value for the current strength may be obtained by this operation, the wires which make the connections 1–1′, 2–2′, etc., must have a resistance equal to that of the amperemeter, while the connections a–1′, a–2′, etc., must be made with wires having practically no resistance. (For further details see p. 122.)

From the electrolytic cells the circuit is completed, on the one hand by wires having extremely low resistances running to the positive pole, and on the other hand by similar wires connected to the binding-posts of the resistance-boxes, or what amounts to the same thing, to the cups s_1, s_2, s_3, s_4. Between one of the latter and the positive pole the tension must be measured, since here the fall in tension is due to the resistance of the cell only. It is accordingly sufficient to make the connection $s_1 - s$, $s_2 - s$, etc., in order to immediately obtain the difference of potential in the corresponding cell. The simultaneous measurement of several cells is of course out of the question.

This simple appliance, the principles of which recur in the following descriptions, can be prepared by anyone from the simplest materials, so that, as already stated, it is very suitable for students, since by working with it they become acquainted with the methods of making connections and the manipulation of more elaborate apparatus.

The resistance-boxes permit of a variation of the tension and current strength sufficient for most purposes.

FORMER EQUIPMENT OF THE ELECTRO-CHEMICAL INSTITUTE AT AACHEN.

This system is based upon the employment of a dynamo of the type described on page 62, the current from which can be employed both directly and for charging accumulators.

As already stated, the machine described has a tension of 10 volts with 1,000 revolutions. The tension, while the machine is in use, is measured by a galvanometer or other instrument which shows the tension directly. In Fig. 81, the tension indicator marked G is connected with both ends of the brass resistance MM_1.

Siemens & Halske describe the tension indicator as follows: It consists of an electro-magnet, beside one pole of which stands on edge a piece of iron which has the same polarity, and is therefore repelled by it in proportion to the strength of the magnetism, and so of the electric current which passes around the instrument. The extent of the repulsion is measured on a scale on which plays an index attached to the piece of iron which is repelled. The indications of the instrument are not entirely independent of the residual magnetism; the direction of the current in the instrument must therefore be always the same. This result is accomplished by a small adjustable permanent magnet in front of the lower pole of the electro-magnet; this shows the direction of the current in the instrument, and stops the index if the current is in the wrong direction. (See Z, Fig. 81.) If this occurs, the wires leading the current to the instrument must be interchanged.

The instrument is supplied with a brass ring, which, before the current passes, is placed on the round weight of the index, and must then turn the index to the zero point. If this is not the case, the instrument is not plumb. When the instrument is in use, the ring is removed.

As already stated, the laboratory apparatus constructed by Siemens & Halske is capable of carrying on, at the same time, a large number of electrolytic determinations on the

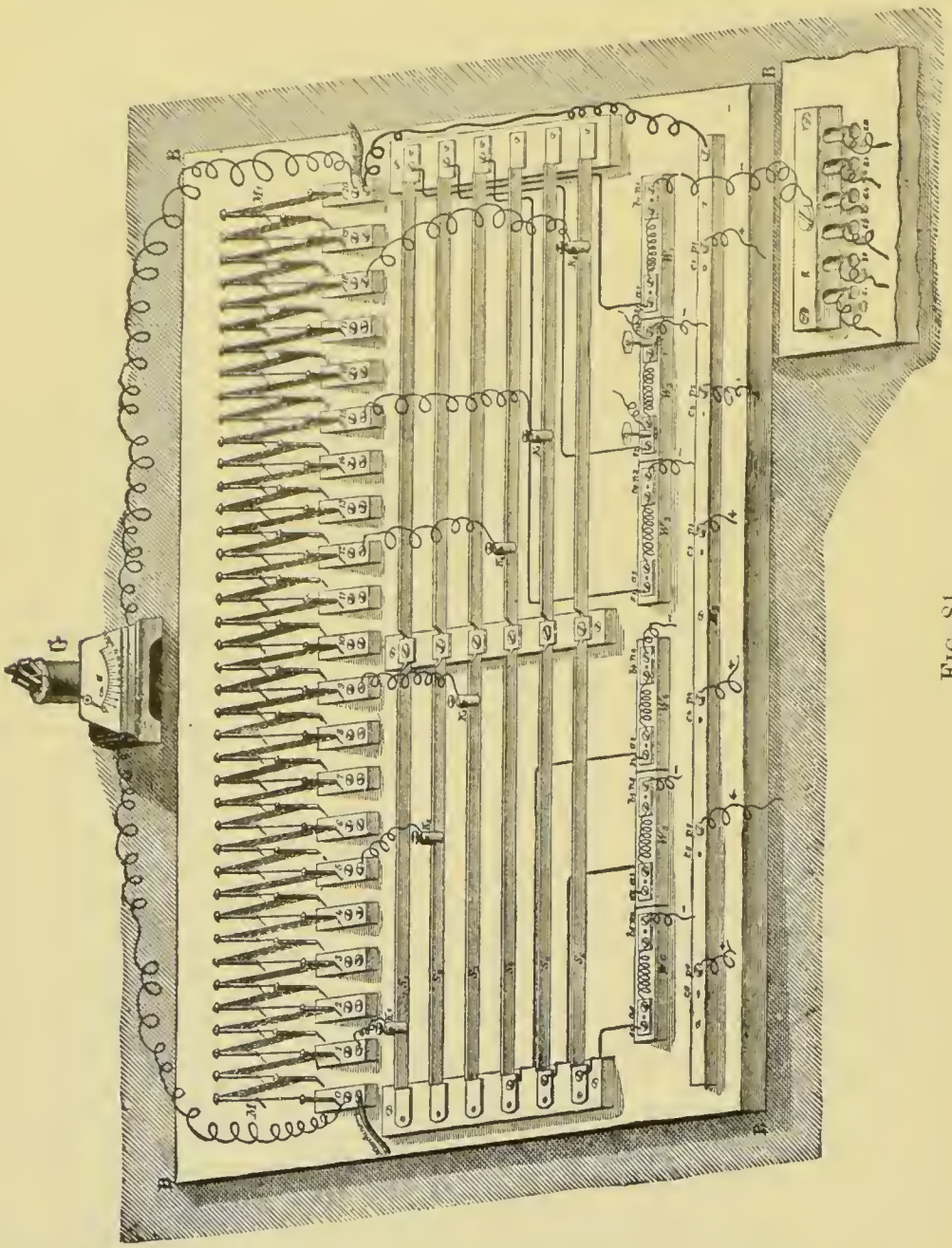


FIG. 81.

small scale, requiring currents differing in strength and tension, so that each determination is independent of the rest. According to the description of Siemens & Halske, this

result is obtained essentially by passing far the greater part of the current through a brass wire-gauze resistance,* the individual determinations being made by small branch currents which may be independently varied in intensity by attaching their conductors to different portions of the wire-gauze resistance.

The dynamo machine is connected by short heavy conductors to the ends $M\,M_1$ of the zigzag brass wire-gauze resistance. These ends of the resistance are also connected, by smaller wires, with the instrument which shows directly the tension at the resistance. Care must be taken that this instrument always shows the same tension, i.e., that the velocity of the machine is uniform. If the tension at the ends of the resistance is 6 volts, and the resistance is made up of 24 equal parts, the ends of which are connected with binding-screws, the difference in tension between any two adjacent binding-screws is $\frac{6}{24} = \frac{1}{4}$ volt. If the tension at the first screw is 0, the tensions at the following screws are $\frac{1}{4}$, $\frac{2}{4}$, $\frac{3}{4}$, 1, $\frac{5}{4}$, etc., volts; that is, the whole interval of 6 volts is divided into portions of $\frac{1}{4}$ volt each.

If, now, a current, small in proportion to the current passing through the resistance, is taken out between any two binding-screws for an electrolytic determination, the tension between the screws is not materially changed; the wires carrying this current can be connected with any binding screws without any change in the main current; moreover,

* When the same source of current is used for carrying on a number of dissimilar experiments simultaneously, the employment of resistances and the loss of a part of the energy is unavoidable. The apparatus constructed by Siemens and Halske has the advantage that it makes use of only a single resistance, while with all other arrangements as many separate resistances are required as experiments are conducted.

the introduction of a number of such currents does not materially change the tension, and the tension for any given determination can be varied at will without affecting the others.

In the apparatus used by the author, Fig. 81 (one-twentieth natural size), the brass wire gauze resistance is divided into 20 equal parts marked 1, 2, 3, etc. As already stated, the machine, at 1,000 revolutions, has a current-strength of 60 amperes and a tension of 10 volts. Of the 60 amperes, 40 are conducted through the resistance, so that 20 remain for electrolytic determinations.

The difference of tension between two adjacent binding-screws is $\frac{10}{20} = \frac{1}{2}$ volt. The tension, that is, at the screw marked 19, is $\frac{1}{2}$ volt, at 18 = 1, at 17 = $1\frac{1}{2}$, at 16 = 2, at 0 = 10 volts.

The current from the machine enters by a heavy copper conductor at the screw marked 0, and passes out at that marked 20.

On the board BBBB are fastened 6 T-shaped galvanized-iron strips, S_1, S_2, S_3, S_4, S_5, S_6, six resistances of 0.1 ohm each, W_1, W_2, W_3, W_4, W_5, W_6 (to allow the strength of current in single experiments to be measured), and the brass strip M_2. S_1 is connected by a wire with W_1, S_2 with W_2, S_3 with W_3, S_4 with W_4, S_5 with W_5, and S_6 with W_6. The iron strips may be connected with the binding-screws 1, 2, 3, etc., by means of wires and the brass screws K_1, K_2, etc. If the apparatus is used as shown in the cut, and 1, 2, or 3 is connected with S_1, 4, 5, or 6 with S_2, 7, 8, or 9 with S_3, 10, 11, or 12 with S_4, 13, 14, 15, or 16 with S_5, and one of the others with S_6, the strongest current is at W_1, and the weakest at W_6. Any strip may, of course, be connected with any binding-screw.

In performing electrolysis, the solutions to be acted on

are placed in connection with a negative pole n_1, n_2, or n_3, etc. (on the resistances W_1, W_2, or W_3, etc.), and a positive pole p_1, p_2, or p_3, etc., on the brass strip M_2, the connections being made according to the strength of current desired.

Moreover, as shown by the examples given later, several determinations requiring the same strength of current may be connected with any pair of poles, n_1 and p_1, n_2 and p_2, etc. In order to connect more conveniently with the platinum dishes containing the solutions for electrolysis, n_1 and p_1, for instance, may be connected with a brass strip Z (the connection with n_1 only is shown in the cut), to which are attached a number of binding-screws, z_1, z_2, etc.

The tension and the strength of the current may be measured at each dish. For example, if the tension at the dish connected with W_2 is to be measured, the plugs from the galvanometer are inserted at b_2 and c_2; if they are inserted at a_2 and b_2, the tension in the resistance is measured, which, multiplied by 10, gives, in amperes, the strength of the current acting on the solution connected with W_2.

In order to test the working of the apparatus, the tension at the divisions of the wire-gauze resistance was directly measured by a torsion galvanometer, with the following results:

Resistance marked	Connected with Binding Screw, marked	Tension in Volts.
W_1	1	10.300
W_1	2	9.900
W_1	3	9.400
W_2	4	8.950
W_2	5	8.300
W_2	6	7.750
W_3	7	7.200
W_3	8	6.650
W_3	9	5.950
W_4	10	5.500
W_4	11	5.050
W_4	12	4.500
W_5	13	4.000
W_5	14	3.450
W_5	15	2.850
W_5	16	2.300
W_6	17	1.700
W_6	18	1.100
W_6	19	0.560
W_6	20	0.007

For the measurement of the strength of the current at the screws 1 to 20, a cell was used which had a copper elec-

trode,* and contained 150 cc. of a 15 per cent solution of copper sulphate, this cell was connected to the resistance W_6 (binding-screws, n_6 and p_6). The screws 1 to 20 were then successively connected with the bar S_6, and the deflection of the galvanometer read, the plugs connecting it being placed in a_6 and b_6. After this reading, the tension in the cell was read, for each screw connection, by placing the plugs in b_6 and c_6.

In order to control the rate of the machine during the experiment, p_1 and n_1 on the resistance W_1 were connected through a rheostat; and the tension at the binding-screw 1 (connected with S_1) was determined by a second torsion galvanometer, the plugs from which were inserted at b_1 and c_1.

The results of these experiments are given in the following table in the columns included under I.

A second series of experiments was conducted to determine the strength of the current by the quantity of copper precipitated.

Six platinum dishes, as nearly alike as possible, were filled with 150 cc each of a 15 per cent solution of copper sulphate, supplied with copper electrodes (see note below), and different quantities of copper precipitated in the same time. These experiments were conducted in three series, as follows: —

Series 1. I., IV., VIII., XII., XVI., XIX.
Series 2. II., V., IX., XIII., XVII., XX.
Series 3. III., VI., X., XI., XIV., XVIII.

---

* The cell consisted of a platinum dish, and the positive electrode was a round piece of sheet-copper (of the form of the platinum electrode shown in Fig. 55), 6 cm. in diameter and 2 mm. thick. The electrodes were 2.5 cm. apart.

Of the columns included under II., A gives the strength of the current as determined from the precipitated copper; B, the results, in a few cases, of the measurement of the strength of current by a torsion galvanometer; and C, the tension measured at the same time with the torsion galvanometer.

Binding Screw.	I.			II.		
	Amperes.	Volts, Experiment.	Volts, Machine.	A, Amperes.	B, Amperes.	C, Volts.
I.	18.018	7.900	10.90	15.97	–	9.200
II.	15.352	7.400	9.90	14.04	–	9.000
III.	13.231	7.100	10.10	10.86	10.800	7.900
IV.	11.615	6.650	10.10	8.87	–	7.400
V.	10.302	6.350	10.30	8.00	–	7.100
VI.	9.595	6.010	10.40	6.04	–	5.500
VII.	8.383	5.710	10.50	–	–	–
VIII.	6.565	5.300	10.60	4.97	–	5.000
IX.	5.757	5.100	10.60	4.21	3.800	4.500
X.	4.747	4.700	11.10	4.03	–	3.800
XI.	4.040	4.250	10.90	3.75	3.700	3.100
XII.	3.838	3.800	11.00	3.54	–	2.900
XIII.	3.535	3.400	10.90	3.47	–	2.500
XIV.	3.030	2.850	10.90	3.09	2.700	2.300
XV.	2.520	2.400	11.05	–	–	–
XVI.	2.120	1.900	11.00	1.85	–	1.200
XVII.	1.560	1.500	11.00	1.35	–	1.050
XVIII.	0.759	0.890	10.90	0.76	0.605	0.600
XIX.	0.396	0.290	11.00	0.54	–	0.360
XX.	0.000	0.007	11.10	0.00	–	0.007

The following sixteen experiments were made simultaneously under the same conditions as before. The numbers in column A express the quantities of copper precipitated in 6.5 minutes; those under B, the tensions measured with the torsion galvanometer.

	A, Copper.	B, Volts.
Binding screw I. to W_1 . .	0.7616 g 0.7415 " 0.8286 "	7.10
Screw IV. to W_2	0.6021 " 0.5716 " 0.4788 "	5.30
Screw VIII. to W_3	0.4155 " 0.3510 " 0.3535 "	3.30
Screw XII. to W_4	0.2648 " 0.2963 " 0.2652 "	1.80
Screw XVI. to W_5	0.1435 " 0.1470 "	0.90
Screw XIX. to W_6	0.0363 " 0.0260 "	0.23

In order to reach a conclusion as to the value of the apparatus for the purposes of quantitative analysis, twelve determinations were carried on simultaneously, at the author's request, by Dr. Robert Ludwig, formerly assistant in the Inorganic Laboratory. The solutions used for these experiments were of iron, cobalt, tin, antimony, and copper, metals

which, as will be shown later, require currents of widely different strengths for their separation. The results of one series of these experiments are subjoined.

	Taken.	Found.
I.	0.3546 g Fe_2O_3	0.2479 g Fe = 0.3541 g Fe_2O_3
II.	0.3836 " Fe_2O_3	0.2691 " Fe = 0.3844 " Fe_2O_3
III.	0.2624 " Co	0.2619 " Co
IV.	0.2234 " Co	0.2231 " Co
V.	0.1145 " Sn	0.1142 " Sn
VI.	0.2290 " Sn	0.2290 " Sn
VII.	0.2025 " Sb_2S_3	0.1444 " Sb = 0.2019 " Sb_2S_3
VIII.	0.1890 " Sb_2S_3	0.1348 " Sb = 0.1885 " Sb_2S_3
IX.	0.1670 " Sb_2S_3	0.1189 " Sb = 0.1663 " Sb_2S_3
X.	0.8374 " $CuSO_4$	0.2133 " Cu = 25.47 % Cu
XI.	0.8768 " $CuSO_4$	0.2225 " Cu = 25.31 % Cu
XII.	0.7905 " $CuSO_4$	0.1991 " Cu = 25.29 % Cu Calculated 25.39 % Cu

In general the current of the dynamo was not directly employed, but was used to charge four accumulators, which sent their current of 8 volts to the electrolytic work-bench. The current thus transformed was employed in the following manner (Table I).

The connection of the cells with the positive conductor, which carries the current of the four accumulators to the electrolytic table, is effected by means of six binding-screws (marked 1, 2, 3, 4, 5, 6). For connecting the cells with the negative pole of the source of current, wooden blocks bearing separate binding-posts and mercury-cups (in the diagram 6) are made use of. The arrangement of such a board is shown in Fig. 82 ($\frac{3}{4}$ actual size).

The cups marked 1, 2, 3, 4 are connected with the four binding-posts K, cups 5 and 6 with the negative conductor

from the source of current, and cup 7 with one conductor from the amperemeter. The connections between the cups are made by plain copper forks while the current is being measured, and otherwise by forks upon which resistances

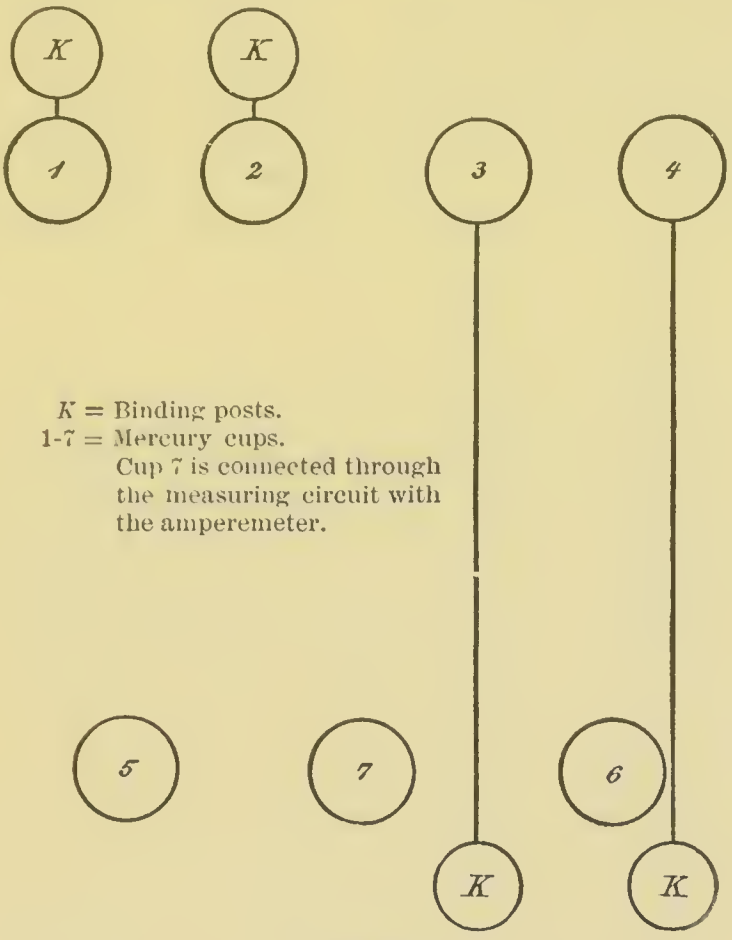


FIG. 82.

equal to the resistance of the measuring instrument are rolled. A fork of this description (resistance-roll) is shown separately in Fig. 83. An instrument made by Hartmann & Braun (Bockenheim-Frankfurt a. M.) serves for measuring the current strength. This instrument, especially constructed for the laboratory of instruction, is provided with two scales and pointers (one on each side), which allow of its being observed from all points on the work-bench. The pointer of the

amperemeter moves over a scale having a radius of 16 cm. The instrument permits of the measurement of currents up to 2 amperes in decimals of 0.05 ampere. By the use of a resistance which may be connected in shunt, the range of measurement is increased tenfold. The resistance of the instrument itself is 0.32 ohm. An exactly equal resistance is contained in the resistance-roll.

The measurement of the current strength in the cell is conducted as follows: A moderately high resistance of, say, 60 ohms is inserted in the circuit of the connected rheostat and a wire from a positive binding-screw is connected with

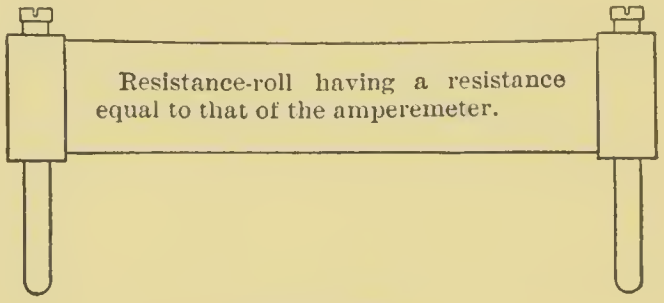


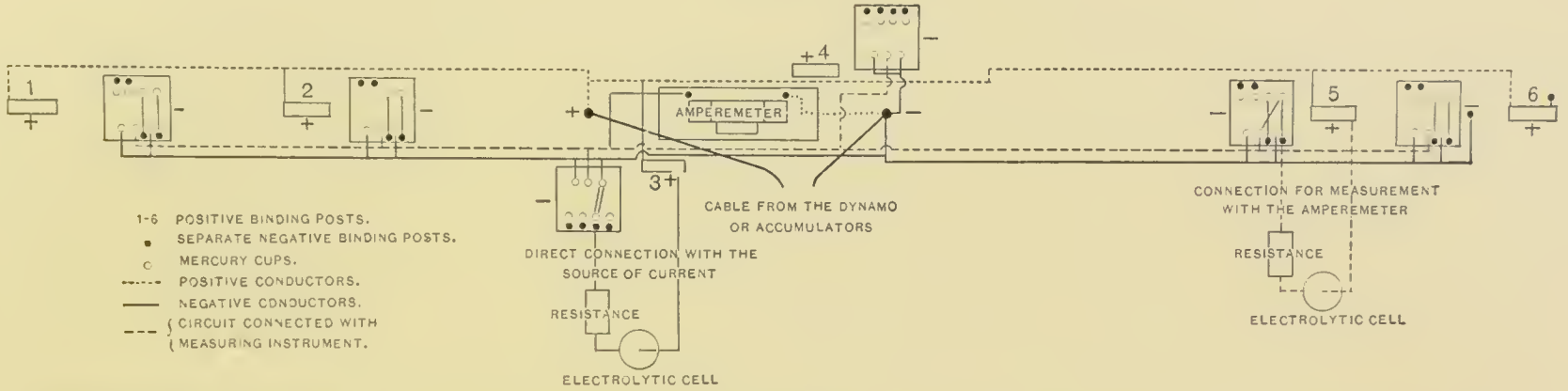
FIG. 83.

the anode of the cell. A wire running to one of the negative binding-screws (for example, 5, Table I, Fig. 1) is now attached through the rheostat to the cathode. The arrangement is seen from Table I, Fig. 1. It only remains to connect the mercury-cups 4 and 7 (the latter connected with the amperemeter) by means of a copper fork. With a resistance of 60 ohms in the circuit the amperemeter will show only a small deflection, which may be increased to the required value by reducing the resistance in the rheostat. This having been done, a resistance-roll is inserted between the cups 4 and 6 and the copper fork between 4 and 7 is removed, which breaks the connection with the amperemeter. Since the resistance of the amperemeter and roll are equal, a current

TABLE I.

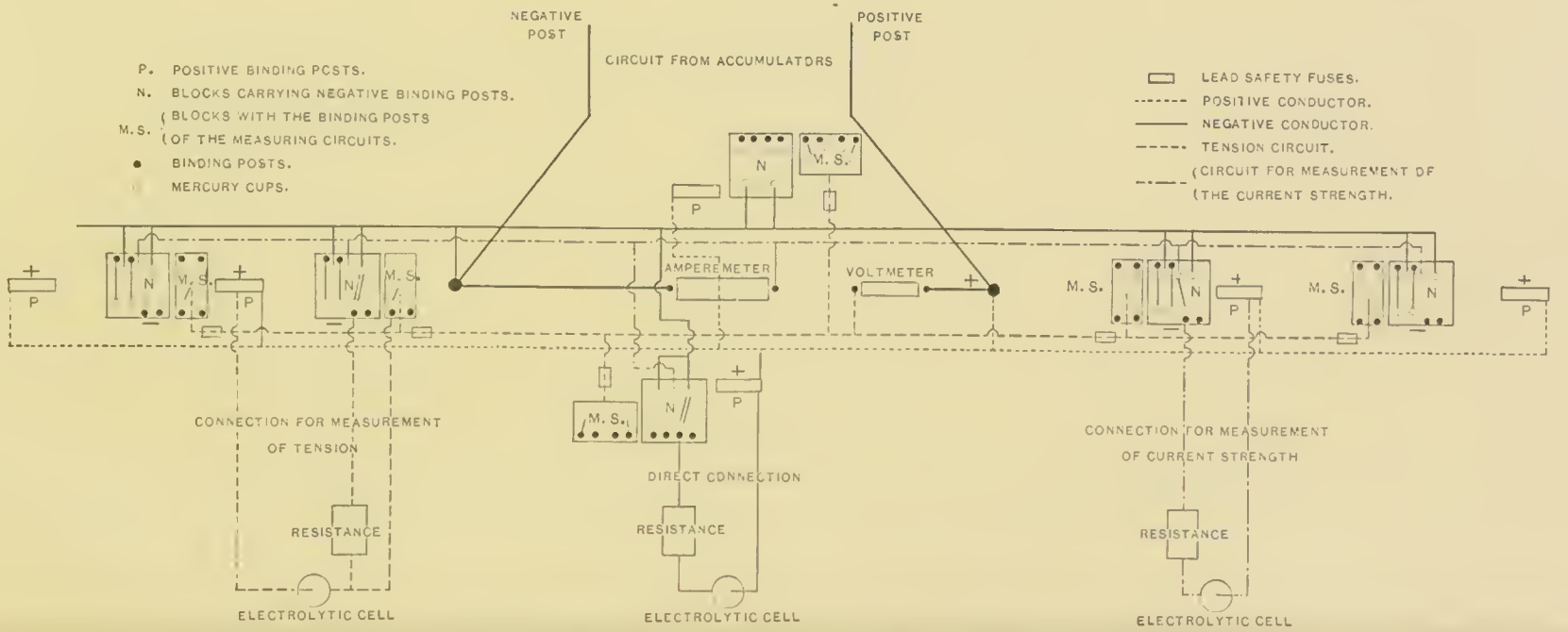
PLAN SHOWING ARRANGEMENT FOR MEASURING THE CURRENT STRENGTH OF EACH SEPARATE ELECTROLYSIS WITH THE USE OF A SINGLE AMPEREMETER.

FIG. 1.



PLAN OF WORK-BENCH IN ELECTROCHEMICAL LABORATORY OF THE ROYAL TECHNICAL HIGH SCHOOL AT AACHEN.

FIG. 2.



FORMER EQUIPMENT OF PRIVATE LABORATORY. See page 123.

corresponding to the one measured flows through the cell. To observe the current strength during the electrolysis, the copper fork is placed in the cups 4 and 7, and the resistance-roll is removed. It is, therefore, possible to measure the current strength at any time without interrupting the current through the cell. As is evident from Table I, Fig. 1, the construction of the electrolytic table allows 24 separate electrolyses to be conducted simultaneously. If at least four accumulators, with a tension of 8 volts, are used, a considerable number of experiments may be carried out at the same time quite independently of one another.

The former equipment of the private laboratory is, without further comment, evident from Table II. It includes a special connection for using the current from the dynamo directly, as well as for working with the 8 accumulators. The wire-gauze resistance, described on p. 113, serves to reduce the current when charging the accumulators, or in the direct employment of the same. The conductors from the dynamo and accumulators pass from the private laboratory to the electrolytic tables in the laboratory of instruction. An amperemeter shows the current which is there being used, while another amperemeter serves to control the current used for charging the accumulators. The complete arrangement of the plant is explained by Table I, Fig. 2.

That accumulators furnish the most suitable source of current for electrolysis is to-day beyond question. These instruments, since they can also be charged with a thermopile, are more practical and convenient for small laboratories than primary batteries, which furnish either insufficient or inconstant currents.

The torsion galvanometer has long served in this laboratory for measuring the tension at the electrodes. Since a knowledge of the tension is of great importance, both for the

quality of the precipitated metal and for the separation of different metals, it must always be possible, as has been repeatedly stated, to determine the tension as well as the current strength. How this may be accomplished with a single voltmeter, in the performance of several simultaneous experiments by means of a common source of current, is clear from the diagram, Table I, Fig. 2.

When this method is used, special care must be taken that the rheostat is connected between the cell and the negative pole, since otherwise the tension of the accumulators and not that of the cell will be measured. In carrying out the measurement, only the cathode should be connected with the voltmeter circuit, if a deflection at the voltmeter is expected. The manner of attaching the cell is readily seen from the sketch. Since the measurement of several tensions cannot be conducted at the same time, owing to one interfering with the other, it must always be ascertained, before switching in the voltmeter, that it is not in use elsewhere.

PRESENT EQUIPMENT OF THE ELECTROCHEMICAL INSTITUTE OF THE TECHNICAL HIGH SCHOOL.

Although the electric current of the former equipment was furnished by an independent generating plant, such is not the case in the present one. It was considered desirable to be as independent of a power plant as possible, since these are by nature uneconomical, and moreover are not always ready for use.

The solution of the problem was made possible by the fact that the city of Aachen has an electric-power station, the cables of which extend to the Technical High School. It was decided, therefore, to take the electricity for the new installation from the city mains.

The current, as taken from the city system, could not, of course, be used for all experiments without modification. As is well known, for carrying out many electro-analyses, only very low tensions, included within the limits 0.5–8 volts, are required.

The current furnished by the Aachen Electrical Works, operating on the three-wire direct-current system, has a tension of about 108 volts between the middle wire and an outside wire, and a tension of about 216 volts between the two outside wires.

It was therefore necessary, in connection with the experiments previously mentioned, to reduce the high tension of the power wire in some suitable manner to the low tension required for experiment. Moreover it should at all times be possible, without special preparation, to carry out experiments with high tension, as for example in experiments where the current must be forced through materials having a high resistance, or for performing experiments with the electric arc.

For the reduction of the high tension to a low tension in the case at hand, a direct-current transformer was considered. The economical working of a double-dynamo combination of this description, its quiet and convenient operation, together with the small space which it occupies, all speak for the choice of the direct-current transformer. The question as to the method of obtaining the low tension required for electrolytic experiments was thus solved.

Before proceeding to the description of the plant installed by the firm of Schuckert & Co., proprietors of the Aachen Electrical Works, the nature of the different experiments and investigations carried out will be briefly sketched in order that what follows may be more readily comprehended.

1. Experiments with Low Tension.

The experiments with low tension are chiefly confined to the electro-analysis of solutions of metallic salts. In addition to this the precipitation of metals on a large scale is also undertaken as an introduction to the study of electroplating.

2. Experiments with High Tension.

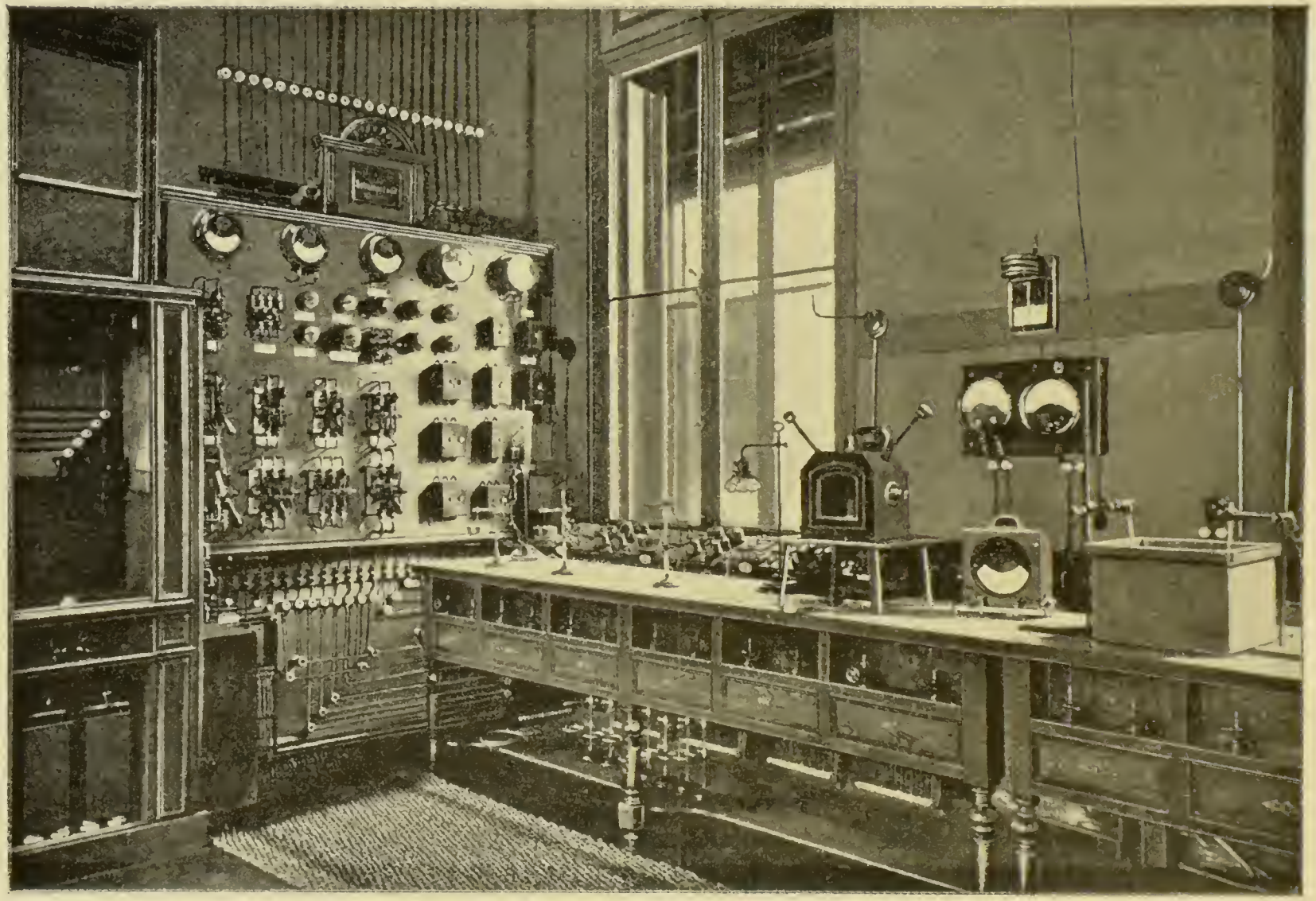
The experiments with high tension begin at about 45 volts, required for the production of the Davy arc; the highest available tension of the supply circuit, that between the two outside wires, is about 216 volts. The high-tension current is chiefly employed for fusion experiments, as well as for the decomposition of gases and other bodies of high resistance.

In addition to the above purposes, the current is also used for running an electric projection lantern, as well as a number of arc and incandescent lights.

The distribution of the current to the various rooms, and also the operation of the transformer, is controlled from a central switchboard. The centralization of the whole plant was desirable for many reasons, chief among which was the fact that a valuable and complicated switchboard might thus be placed under competent supervision in a room not open to every one. This would prevent unauthorized persons from taking off current, and besides would allow a general supervision of the whole plant.

From the central switchboard currents are carried to the following places:

1. Private laboratory.
2. Large lecture-room.
3. Laboratory for electro-analysis.



PRESENT EQUIPMENT OF PRIVATE LABORATORY. See page 127.

4. Laboratory for experiments on a large scale with high and low tension.

The circuits running to the different rooms are distinguished, according to the purpose for which the current they carry is intended, as:

a. Lighting circuits,
b. High-tension circuits,
c. Low-tension circuits,

and are entirely independent of one another.

The lighting circuits run to the private laboratory and to the large lecture-room.

The circuits for the high-tension current extend to the private laboratory, to the large lecture-room, and to the laboratory for experiments with high- and low-tension.

The circuits for low-tension current extend to the private laboratory, the large lecture-room, the laboratory for electro-analysis, and the research room for high and low tension.

In addition to the above circuits, which are intended for direct current transmission, there are also to be mentioned the circuit for charging the two batteries of accumulators and the circuit for running the transformer.

The switches, resistances, controlling, and measuring apparatus belonging to the different circuits are located on the central switchboard.

1. Private Laboratory.

Concerning the special arrangements, the private laboratory will next be mentioned. As already stated, the central switchboard, with the apparatus for the control of the whole plant, is placed in the private laboratory. In this room there is also located a battery of accumulators.

Table III gives a photographic view showing the arrangement of this laboratory. In the middle may be seen the

central switchboard upon which the various instruments are mounted; to the left stands the glass closet containing the battery of accumulators. On the wall by the window are two work-benches, one intended especially for electro-analytical work with low tensions and small currents, and the other for experiments with high tensions and large currents.

The arrangement for electro-analysis is as follows: On the back of the corner bench is a slanting wooden frame, on the face of which are fastened the switches and branch binding-posts, while the connecting wires are attached to the back. There are altogether five work-places on this bench, each of which will permit of the performance of two analyses simultaneously, so that in all ten experiments may be carried on at the same time.

The installation of these work-places, as well as of the second work-bench, is in accordance with the scheme for current distribution shown in Table IV.

Each work-place is connected in parallel to the positive and negative conductors, which are run through the work-bench.

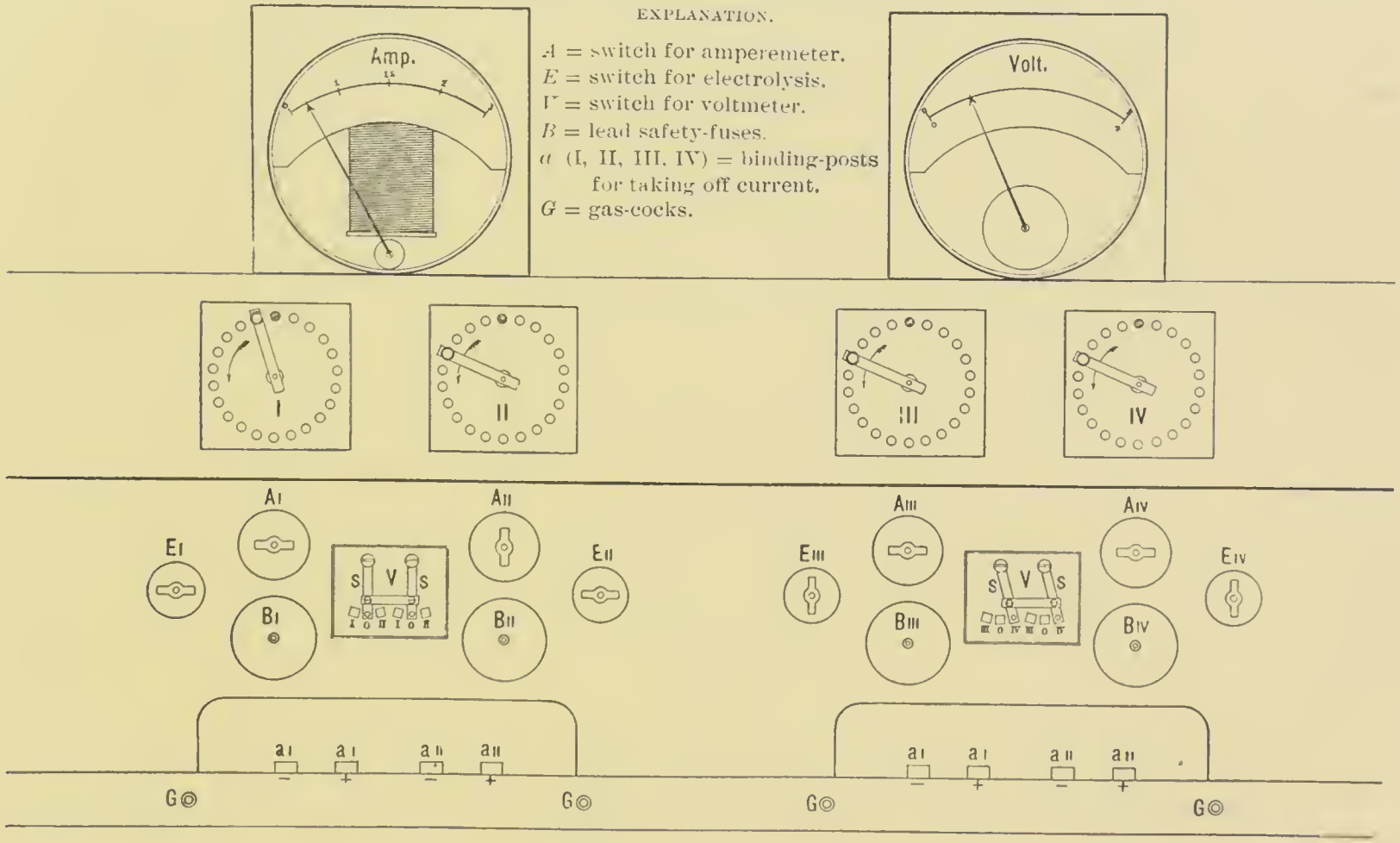
The current for every analysis can be independently varied by means of the regulating resistance at the work-place. A single amperemeter, which can be thrown into the circuit of any analysis by means of a switch placed at each work-place, serves for measuring the current strength. When the amperemeter is cut out, its place is taken by a resistance, in order that the current strength may not be altered (see p. 122).

The measurement of the tension is carried out in a similar manner by a single voltmeter, which may at will be switched into the circuit of any analysis in operation.

A lead safety fuse is inserted in the circuit of each of the ten branches, to guard against the possibility of too great current strength.

TABLE IV.

PLAN OF SEPARATE INSTRUMENTS ON LABORATORY WORK-BENCH.



EXPLANATION.

A = switch for amperemeter.
E = switch for electrolysis.
V = switch for voltmeter.
B = lead safety-fuses.
a (I, II, III, IV) = binding-posts for taking off current.
G = gas-cocks.

The connections of the electrolytic apparatus to the small switchboards of the work-bench are made with very flexible rubber-insulated copper leads, the ends of which are provided with small copper links to allow of a more convenient attachment to the apparatus.

For setting up experiments where large currents of high or low tension are required, two cases furnished with locks are affixed to the second work-bench. That for low tension contains two branch plates which carry a number of binding-posts, thus allowing several different pieces of apparatus to be connected at the same time.

The case for high tension contains three plates, connected with the two outside leads and the middle lead of the three-wire system respectively, whereby a maximum tension of about 216 volts is obtainable. These plates also carry several binding-posts, which permit the use of several pieces of apparatus at one time.

The two accumulator batteries are comprised of four cells each. One battery, with the cells connected in series, requires a charging current of 90 amperes; the other, similarly connected, requires 25 amperes.

The batteries are charged from the transformer.

The small battery furnishes current to the private laboratory only, while the large one supplies the rest of the plant. Each of the batteries is provided with a cell switchboard for four cells, so that by cutting out separate cells the tension of the current may be reduced and the use of high external resistances avoided.

As a protection against the possibility of the current reversing during the process of charging, and flowing back through the transformer, each battery circuit is provided with an automatic cut-out.

The tension of the separate cells is controlled by a special

voltmeter having contact plugs, which allows the tension of each cell to be independently measured at the cell switchboard.

For the measurement of the battery tension and the strength of the charging and discharging currents a special voltmeter and amperemeter are provided. Further, that the operation of charging and discharging may be more closely observed, indicators for showing the direction of the current are attached to the corresponding circuits.

2. Large Lecture-Room.

The installation of the large lecture-room is especially intended for the performance of lecture experiments, which comprise the demonstration of electrolysis, the decomposition of gases and liquids by the Davy arc, and fusion experiments.

Besides this, provision is made for the running of an electric projecting lantern, as well as for a number of incandescent and arc lamps.

3. Laboratory for the Electro-analysis of Metals.

In this room the transformer is placed. It also contains a large experiment table having ten work-places, for carrying out electro-analytical experiments with low tensions. (Cf. Table V.)

The transformer will next be described. This consists of a combination of two direct-current dynamos, with their shafts coupled directly together. One of the dynamos, arranged as a motor, is driven by the current from the two outside wires of the three-wire system, by a tension, therefore, of about 216 volts. The circuit is run to the transformer from the central switchboard. The dynamo which is coupled to the motor, and which furnishes the low-tension

WORK-BENCH IN LABORATORY FOR ELECTRO-ANALYSIS. See page 130.

current, is so arranged that the tension at the poles may be varied from about 4.5–9 volts, the corresponding current strengths being respectively 360 and 180 amperes. The conductors carrying the low-tension current from the dynamo run to the central switchboard. The tension of 9 volts is the one generally used, the lower tension of 4.5 volts being employed for larger electrolytic experiments, such as the preparation of pure metals.

The alteration in the tension of the current is brought about by connecting the two halves of the double armature, with which the transformer is provided, either in series or in parallel. This is done by merely changing the corresponding connections on the frame of the transformer.

Further concerning the construction of the transformer, it should be mentioned that the machine is very solidly cast, and the magnets protected within the frame, so that a mechanical injury to the magnet-coils is out of the question. The lubrication of all parts is carried out by means of ring-lubrication, which has proved very satisfactory. Such delays as often occur when other mechanical contrivances are employed are here impossible. Owing to its construction, the transformer, which for protection is enclosed in a special covering, can run for hours without particular attention.

The action of the transformer, in spite of its speed of about 1300 revolutions per minute, is so quiet and free from any jarring or shaking, that its running can scarcely be detected even in the immediate neighborhood.

It should be stated that there is a switchboard near the transformer, by which direct currents of low tension can be taken off in this room, without making use of the central switchboard. Such currents are required when experiments with high current strength and low tension are performed;

and in such cases short cables are run from this switchboard to the nearest work-bench, where the apparatus is set up.

The arrangement of the large work-bench, a photograph of which is given in Table V, corresponds in general to that of the table for conducting analyses in the private laboratory.

Here, on either side of the bench, there are five work-places, each of which allows of the simultaneous performance of two analyses, so that in all twenty experiments may be carried on at the same time.*

Table IV shows the method employed for measuring the current strength and tension of an analysis. The amperemeter and voltmeter are above. The current strengths are regulated by means of the rheostats (I, II, III, and IV). These consist of slate slabs into which are fixed metal knobs, which are attached to separate resistance spirals. By turning the lever in the direction indicated by the arrow, the resistance is cut out and the current strength correspondingly increased.

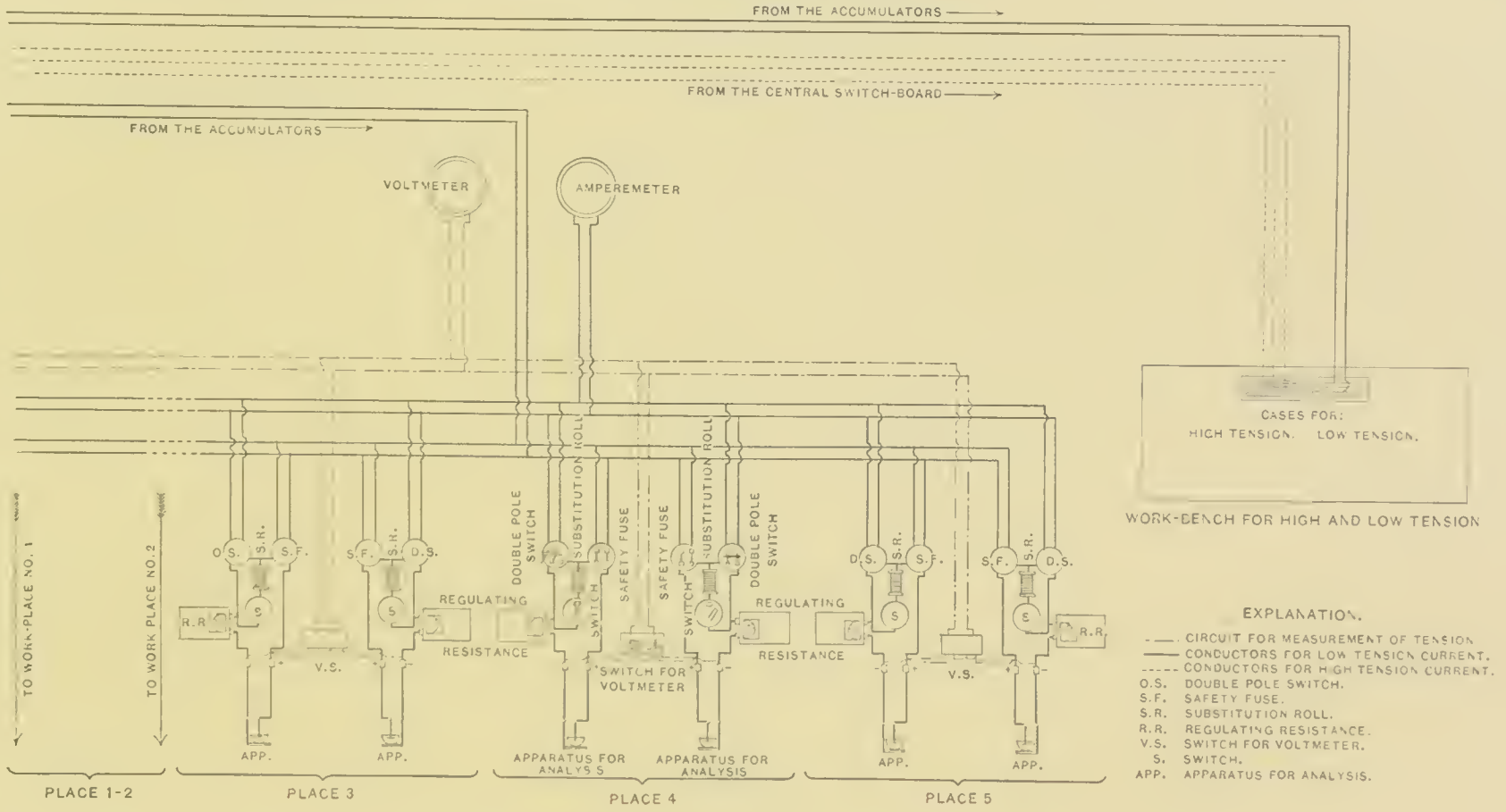
The switches for the amperemeter $A_{(I, II, III, IV)}$, for the electrolyses $E_{(I, II, III, IV)}$, and the safety-fuses $B_{(I, II, III, IV)}$ are located under bronzed metal cases.

$a_{(I, II, III, IV)}$ are the binding-posts to which the electrolyses are connected, V is a double-pole switch used in measuring the tension. In the position o the voltmeter is cut out; at I, II, III, IV the corresponding electrolysis is connected with the voltmeter. As already stated, there is only one amperemeter and one voltmeter to every table with 10–20 dishes, and therefore only one electrolysis can be measured at a time. The four figures on Table IV are designed to make the explanations clearer.

* Two other work-benches have been recently added, so that there are now twenty work-places for electro-analysis.

TABLE VI.

PLAN SHOWING CURRENT DISTRIBUTION ON WORK-BENCH, ELECTROCHEMICAL LABORATORY OF ROYAL TECHNICAL HIGH SCHOOL, AACHEN.



In position I, where the keys A_I and E_I are horizontal, the circuit is closed. In II, A_{II} is perpendicular; the amperemeter is in circuit. The lever of the rheostat at II may be turned in the direction of the arrow until the measuring apparatus registers the desired current strength. A is then brought into the position A_{III} and E to E_{III}. The current now flows no longer through the amperemeter, but through a roll of wire, the resistance of which is equal to that of the amperemeter. The current strength remains the same as that previously shown by the amperemeter.

V serves for measuring the tension at the poles of the electrolytic vessel, as shown at V_{IV}. In this operation the position of A and E is the same as in III. The two metal strips (SS) are pushed to the right or left (in the figure to the right, iv), whereupon the voltmeter shows the tension existing at that time at the poles of the corresponding electrolysis. The instruments should be cut out immediately after use.

4. Laboratory for Performing Experiments on a Large Scale with Low and High Tensions.

As already mentioned, special cases which receive their currents from separate conductors running from the central switchboard are arranged for high and low tension.

Within the case for high tension there are three separate plates corresponding to the three wires of the three-wire system, providing currents at tensions of 108 and 216 volts accordingly.

The case for low tension contains two connections, with possible tension at the poles up to 9 volts.

From both of the cases separate branch circuits run to the four work-benches, where they end in terminal boxes pro-

vided with locks. By this arrangement each table is provided with both high and low tension.

Each of the branches running to the tables is supplied with a safety fuse and a switch; each table is therefore independent of the others.

A set of transportable resistances and measuring instruments for regulating the current is used in carrying out experiments.

Large and cumbersome resistances are required to produce appreciable variations in the tension. A simple appliance in use in the Aachen laboratory overcomes this difficulty in the case of experiments of short duration, where economical use of the current is not an essential feature. This scheme, originated by Löb and Kaufmann,* permits the convenient splitting up of the current of 216 or 108 volts into separate independent currents having the required lower tension.

A number of lead plates are hung parallel to one another in a large porcelain trough filled with sulphuric acid (Fig. 84), in such a manner that they cut all the lines of the current. They must therefore almost touch the sides and bottom of the trough. When the current passes, these lead plates act as intermediate conductors, the sum of their separate tensions being equal to the tension of the main current. The arrangement is of course impractical as an accumulator, since the polarized plates immediately short-circuit through the electrolyte and are reduced to the potential of the electrodes.

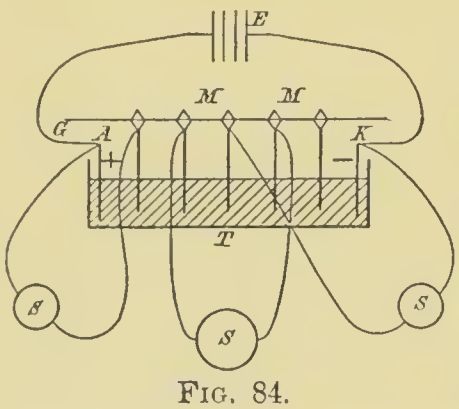


FIG. 84.

* Zeitschr. f. Elektroch., 1895–96, p. 345. *Ibid.*, p. 664.

The immersed lead plates can be slid along the length of the trough on the glass rod by which they are hung. By moving the plates toward or away from the electrodes the tension is varied, and any desired tension may be obtained by making a connection between a terminal electrode and one of the plates. The arrangement is given in Fig. 84. E denotes the source of current; T, the trough filled with sulphuric acid; A and K, anode and cathode; M, the five plates. The wires to S show the removal of three separate currents of different tensions. A large number of such connections are possible. On account of the gases given off, the trough should be kept under a hood.

In addition to the details of the equipment which have been described, some general facts in connection with the management of the entire plant should be stated.

Since the apparatus is much used, and is not always placed in experienced hands, it was considered desirable to have all parts solidly constructed and intended for continuous use.

The switches and regulating instruments, as well as the branch plates, are all mounted on bases of fire-proof material.

All connections are made with the best rubber-covered wire, fastened to large porcelain brackets, so that most perfect insulation of the conductors is assured.

To secure against improper use, all switch-cases are provided with safety-locks, so that currents can nowhere be taken off without the permission of the director of the laboratory.

Section II.

SPECIAL PART.

QUANTITATIVE DETERMINATION OF THE METALS.*

IRON.

LITERATURE:

Wrightson, Zeit. f. analyt. Chem., **15**, 305.
Luckow, Zeit. f. analyt. Chem., **19**, 18.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622.
Classen, Zeit. f. Elektrochemie, vol. I.
Moore, Chem. News, **53**, 209.
Smith, Amer. Chem. Jour., **10**, 330.
Brand, Zeit. f. analyt. Chem., **28**, 581.
Drown and Meckenna, J. of Analyt. and Applied Chem., **5**, 627.
Smith and Muhr, *ibid.*, **5**, 488.
Rüdorff, Zeit. f. angew. Chem., **15**, 198.
Vortmann, Monatshefte f. Chem., **14**, 542.
Heidenreich, Ber. deutsch. chem. Ges., **29**, 1585.

If the solution of a ferrous salt† is treated with potassium

* Of the methods existing in the literature, reference will be made only to those which give the necessary and complete details concerning the conditions of experiment.

† As stated on p. 5, sulphates are best adapted to this treatment, chlorides less so, while nitrates must be avoided. The presence of phosphoric acid is not harmful.

or ammonium oxalate, there is produced an intensely yellowish-red precipitate of ferrous oxalate, soluble in an excess of the reagent to a yellowish-red solution of the double salt.

The above-named oxalates do not precipitate ferric salts; but, if added in sufficient quantity, a solution of the double ferric salt is produced having a more or less green color. If this solution is submitted to electrolysis, there is first produced the double ferrous salt, which is then decomposed with separation of metallic iron; the green liquid therefore becomes first red, and then colorless. Because of this action, the determination of iron is more rapidly performed in solutions of ferrous than of ferric salts. Potassium iron oxalate is not adapted to electrolysis, because the potassium carbonate which is produced precipitates iron carbonate, and thus complete reduction is prevented. The electrolysis of the ammonium double salt, when ammonium oxalate is in sufficient excess, proceeds smoothly, with no separation of an iron compound. If the solution contains free hydrochloric acid, it is best to remove it by evaporation on the water-bath.

Free sulphuric acid may be neutralized with ammonia, since the ammonium sulphate thus produced only increases the conductivity of the solution. Nitrates are converted by evaporation with sulphuric acid into sulphates, or by repeated evaporation with hydrochloric acid into chlorides.

The determination is conducted as follows: Assuming that 1 g of iron may be present in the solution to be electrolyzed, 6–8 g of ammonium oxalate are dissolved by heat in as little water as possible, and the iron solution is gradually added, with constant agitation.* The solution is then diluted

* It is not desirable to add ammonium oxalate solution to a ferrous solution, as difficultly soluble ferrous oxalate separates, and can be dissolved to the double salt only by long heating. With a ferric solution this precaution is unnecessary.

with water to 100–150 cc, and the positive electrode is immersed in the liquid until it is just covered by the solution. The electrolysis is conducted according to the special directions which are given below.

The end of the reaction is determined by taking out a small portion of the colorless solution with a capillary tube, acidifying strongly with hydrochloric acid, and testing with potassium sulphocyanate. When the reaction is ended the positive electrode is removed from the solution, which is poured off, and the dish washed three times with *cold* water (about 5 cc each time), and three times with absolute alcohol, dried a few moments in the air-bath at a temperature of 70° to 90°, and weighed after cooling.

The separated iron has a steel-gray color and brilliant lustre, is firmly attached to the dish, and can be preserved in the air without oxidation for a full day.

CONDITIONS OF EXPERIMENT.*

Temperature of the liquid: Although the maintenance of a certain uniform temperature is not essential to the success of the experiment, it has been found in practice that the ordinary temperature of the solution (20–40°) is the most favorable to the rapid completion of the analysis.

Current density, ND_{100}: For solutions at ordinary temperature, 1–1.5 amp.; for warm solutions (40–65°), 0.5–1 amp.

Electrode tension: For warm solutions, with the stated current density, 2.0–3.5 volts; otherwise, 3.6–4.3 volts.

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* Method of the author. In all of the author's methods the statements refer to the use of the electrodes described on p. 85; the current densities refer only to the dish given in Fig. 54.

For the quality of the precipitated metal, polished or roughened dishes answer equally well.

EXPERIMENT.

Used 2.1–2.5 g $FeSO_4(NH_4)_2SO_4.6H_2O$, 6–8 g ammonium oxalate, 120 cc of liquid.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.*
1 –1.5	3.85–4.3	20–40°	2 hr. 15 m.	14.21 %
1 –1.05	3.6 –4.2	36°	3 " 50 "	14.21 "
1 –1.08	3.05–3.52	65°	2 " 30 "	14.28 "
0.5–0.55	2.0 –2.3	50–52°	3 " 30 "	14.24 "

Used 2.6–2.8 g ferric potassium oxalate ($Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$), 6–7 g ammonium oxalate.

1.5–1.7	3.55–4.25	35–40°	2 hr. 54 m.	11.39 %†
1.0–1.1	3.9 –4.0	30–40°	3 " 15 "	11.35 "
0.5–0.8	2.4 –2.8	50°	6 " 15 "	11.25 "

Edgar F. Smith precipitates iron from a solution of ammonium citrate to which a few drops of citric acid have been added. The author's experiments in earlier years on the separation of iron from other metals in citric and tartaric acid solution, demonstrated that in the presence of fixed organic acids the precipitated metal always contains carbon. Heidenreich has recently shown, by experiments conducted in the Aachen laboratory, that iron may be quantitatively determined under certain conditions, namely: 0.2 g ferrous ammonium sulphate, 50 cc of a 10 per cent solution of sodium citrate, 2 cc of a saturated solution of citric acid; entire volume of liquid, 120 cc; temperature of room; $ND_{100} = 0.75–0.9$ amp.; electrode tension, 5 volts; time, 4–6 hours. The iron, however, always contains carbon.

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* [Theory 14.29%.] † [Theory 11.40%.]

COBALT.

LITERATURE:

Gibbs, Zeit. f. anal. Chem., **3**, 336; **11**, 10; **22**, 548.
Merrick, Amer. Chemist, **2**, 136.
Wrightson, Zeit. f. anal. Chem., **15**, 300, 303, 333.
Schweder, *ibid.*, **16**, 344.
Cheney and Richards, Amer. Jour. of Science and Arts, [3] **14**, 178.
Ohl, Zeit. f. anal. Chem., **18**, 523.
Luckow, *ibid.*, **19**, 314.
Riché, *ibid.*, **21**, 116.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622, 2771.
Classen, *ibid.*, **27**, 2061; Zeit. f. Elektrochemie, 1894–95, Heft 1.
Schucht, Zeit. f. anal. Chem., **21**, 493.
Kohn and Woodgate, Journ. Soc. Chem. Indust., **8**, 256.
Rüdorff, Zeit. f. angew. Chemie, 1892, p. 6.
Brand, Zeit. f. anal. Chemie, **28**, 588.
Le Roy, Compt. rend., **112**, 722.
Vortmann, Monatsh. f. Chem., **14**, 536.
Oettel, Zeit. f. Elektrochemie, 1894–95, p. 195.
Fresenius and Bergmann, Zeit. f. anal. Chem., **19**, 329.

Cobalt may be very easily precipitated from a solution of cobalt ammonium oxalate containing an excess of ammonium oxalate (method of the author). The metal separates rapidly at the negative electrode, in a compact adherent coating, showing its characteristic metallic properties. The operation is performed as in the determination of iron. 4–5 g ammonium oxalate are dissolved by heating in the solution, the volume of which should be about 25 cc; it is then diluted to 100–120 cc, warmed, and electrolyzed at 60–70°.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: The period of electrolysis is considerably shortened by warming, so that a temperature of 60–70° is suitable.

Current density: The proper current density for warmed solutions is $ND_{100} = 1$ amp.

Electrode tension: 3.1–3.8 volts.

The condition of the surface of the cathode has no effect upon the quality of the precipitated metal.

EXPERIMENT.

Used 2.2–2.6 g $CoSO_4.K_2SO_4.6H_2O$, 4–5 g ammonium oxalate, 120 cc solution.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.*
1 –1.1	3.1 –3.78	60–65°	2 hr. 15 m.	13.36 %
0.5–0.52	2.7 –2.95	60–65°	3 " 30 "	13.49 "
1 –1.2	3.9 –4.1	15–35°	4 " 30 "	13.43 "
0.5–0.53	3.46–3.9	15–27°	6 " 35 "	13.25 "

According to a method given by Fresenius and Bergmann, the cobalt solution, after the addition of 15–20 cc of an ammonium sulphate solution (300 g $(NH_4)_2SO_4$ to the liter) and 40 cc ammonia sp. g. 0.96 (where more than 0.5 g cobalt is present in the solution, 50–60 cc NH_4OH), is diluted with water to 150–170 cc, and electrolyzed with a current of $ND_{100} = 0.7$ as a maximum at ordinary temperatures. The presence of chlorides and nitrates is unfavorable to the reduction. Fixed organic acids (citric acid, tartaric acid) and also magnesium compounds act injuriously.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: The separation is not hastened by warming.

Current density: $ND_{100} = 0.5–0.7$ amp.

Electrode tension: With the given current density and at ordinary temperatures, this equals 2.8–3.3 volts.

F. Oettel proposes the following method for the determination of cobalt: The salt is dissolved in water and a quantity

* [Theory 13.43%.]

of ammonium chloride, equal to four times the weight of the salt taken, is added. The volume of the liquid is 150 cc, $\frac{1}{5}$ of which is an ammonia solution (sp. g. = 0.92). After electrolyzing for 14 hours the cobalt is quantitatively precipitated if 100 cc of solution do not contain more than 0.25 g of the cobalt salt.

NICKEL.

LITERATURE:

Gibbs, Zeit. f. anal. Chem., **3**, 336; **11**, 10; **22**, 558.
Merrick, Amer. Chemist, **2**, 136.
Wrightson, Zeit. f. anal. Chem., **15**, 300, 303, 333.
Schweder, *ibid.*, **16**, 344.
Cheney and Richards, Amer. Journ. of Science and Arts, [3] **14**, 178.
Ohl, Zeit. f. anal. Chem., **18**, 523.
Luckow, *ibid.*, **19**, 314.
Richè, *ibid.*, **21**, 116.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622, 2771.
Classen, *ibid.*, **27**, 2061; Zeit. f. Elektrochemie, 1894–95, Heft 1.
Schucht, Zeit. f. anal. Chem., **21**, 493.
Kohn and Woodgate, Journ. Soc. Chem. Indust., **8**, 256.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 6.
Brand, Zeit. f. anal. Chem., **28**, 588.
Le Roy, Compt. rend., **112**, 722.
Vortmann, Monatsh. f. Chemie, **14**, 536.
Campbell and Andrews, Journ. Am. Chem. Soc., **17**, 125.
Oettel, Zeit. f. Elektrochemie, 1894–95, p. 192.
Fresenius and Bergmann, Zeit. f. anal. Chem., **19**, 320.

Nickel may be reduced under conditions similar to those requisite for cobalt; the metal is precipitated from the solution of the double oxalate containing ammonium oxalate in excess, by the action of a similar current, as a thick, bright coating on the negative electrode. The end of the reaction is ascertained by testing with ammonium sulphide or potassium sulphocarbonate, and the precipitate is treated as previously directed.

CONDITIONS OF EXPERIMENT.

The conditions of experiment are the same as in the separation of cobalt. Here also polished or roughened dishes serve equally well.

Used 1.2–2.1 g $NiSO_4.(NH_4)_2SO_4.6H_2O$, 4–5 g ammonium oxalate, 120 cc liquid.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.*
0.9–1	3.1 –2.9	65–70°	2 hr. 50 m.	15.13 %
0.5–0.6	3.38–3.4	17°	5 "	15.11 "
0.9–1	4.09–4.35	15–30°	3 " 35 "	15.05 "
0 5–0.53	2.7 –2.85	60–65°	4 "	15.17 "

The condition of the precipitate is best when the electrolysis is conducted at a temperature of 60–70°, with a current of $ND_{100} = 1$ amp.

According to Fresenius and Bergmann, nickel, like cobalt, may be precipitated completely from a solution treated with ammonium sulphate and ammonia (see Cobalt).

The method given by Oettel for the determination of cobalt may also be used for nickel. For this purpose the nickel salt is dissolved in 20–40 cc ammonia (sp. g. = 0.92) to which 10 g ammonium chloride are added, and after diluting to about 120 cc, the nickel is precipitated in 7–8 hours with a current of $ND_{100} = 0.45$ amp.

Campbell and Andrews dissolve nickel hydroxide in 30 cc of a 10 per cent solution of di-sodium phosphate, to which 30 cc of a concentrated ammonia solution are added, and, with a distance of 5 mm between the electrodes, separate out the nickel by the use of a current of $ND_{100} = 0.14$ amp.

ZINC.

LITERATURE:

Wrightson, Zeit. f. anal. Chem., **15**, 303.
Parodi and Mascazzini, Ber. deutsch. chem. Ges., **10**, 1098; Zeit. f. anal. Chem., **18**, 587.

* [Theory 14.87% Ni.]

Richè, Zeit. f. anal. Chem., **17**, 216.
Beilstein and Jawein, Ber. deutsch. chem. Ges., **12**, 446; Zeit. f. anal. Chem., **18**, 588.
Richè, Zeit. f. anal. Chem., **21**, 119.
Reinhardt and Ihle, Journ. f. prakt. Chem., **24**, 193.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622.
Classen, *ibid.*, **27**, 2060.
Gibbs, Zeit. f. anal. Chem., **22**, 558.
Luckow, *ibid.*, **25**, 113.
Brand, *ibid.*, **28**, 581.
Warwick, Zeit. f. anorg. Chem., **1**, 290.
Vortmann, Ber. deutsch. chem. Ges., **24**, 2753.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 197.
Vortmann, Monatsh. f. Chemie, **14**, 536.
Jordis, Zeit. f. Elektrochemie, 1895–96, pp. 138, 565, 655.
Millot, Bull. de la Soc. chim., **37**, 339.

The metal may be easily and quickly separated from the double salts of zinc ammonium oxalate and zinc potassium oxalate (method of the author).*

The reduced metal has a bluish-white color, and under proper conditions adheres firmly to the negative electrode. Indeed, the metallic zinc often adheres so firmly to the platinum dish that, after being cleaned with water and alcohol, and dried, it is with difficulty dissolved by warming with acids. Generally, after this operation, a dark coating of platinum-black remains which can only be removed by igniting the dish and again treating with acids. It is therefore desirable, before weighing the dish, to precipitate upon it a thin coating of copper, tin, or, better, silver. In laboratories

* The reduction of zinc from a solution of zinc ammonium oxalate is very often credited to Reinhardt and Ihle. The author, however, described this method in Fehling's "Handwörterbuch" before the research of the above-named investigators appeared in the Journal für praktische Chemie, to the editor of which, Kolbe, the author especially stated the facts at the time.

in which many zinc determinations are performed, silver dishes may be advantageously employed.

A bright, thick coating of copper can be obtained in a few minutes if a saturated solution of copper sulphate is treated with an excess of ammonium oxalate to form the double salt, acidified with oxalic acid, warmed to 70–80°, and decomposed by a current of 1 ampere. The preparation of the double salt in a beaker, and the transfer of the clear, hot solution to the platinum dish, is to be recommended.

For silvering the dish it is best to precipitate the silver from a solution of the same in potassium cyanide (see Silver).

In determining zinc by this method, the zinc salt is dissolved in a little water by warming, about 4 g of potassium oxalate or an equal amount of ammonium oxalate is added, and the whole is brought into solution by warming and, if necessary, by the addition of small quantities of water.* The liquid is now transferred to a platinum dish coated with copper or silver, and electrolyzed. The author has demonstrated by experiments that the separation of the zinc in a dense, shiny condition is possible if the solution be kept acid during the process of analysis.

For acidifying the solution, a cold saturated solution of oxalic acid, or, better, a solution of tartaric acid (3 : 50) is employed. At the start the solution is electrolyzed for about 3–5 minutes without addition of acid, and then the acid is permitted to flow in drops (about 10 drops per minute) from a burette with a fine outlet, upon the watch-glass covering the dish. The acid flows through the holes in the watch-glass into the dish itself. After the reduction is completed

* If the alkali oxalate be added to a dilute solution of a zinc salt, there first forms a precipitate of zinc oxalate which is not completely converted into the soluble zinc double salt if the solution of the alkali oxalate is too dilute.

(this is determined with potassium ferrocyanide), the metal must be washed without interrupting the current.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: This must be from 50–60°.

Current density: $ND_{100} = 0.5–1$ amp.

Electrode tension: 3.5–4.8 volts.

Roughened or polished dishes answer equally well.

Time: About 2 hours.

EXPERIMENT.

Used 1.8–2 g zinc ammonium sulphate, 4 g potassium oxalate, 120 cc liquid.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.*
0.5-0.55	3.5–4.0	55–60°	2 hr.	16.44 %
0.9-1	4.7–4.8	60°	1 " 50 m.	16.42 "

According to v. Miller and Kiliani, 4 g potassium oxalate and 3 g potassium sulphate are dissolved in water, the neutralized zinc solution (sulphate or nitrate containing not more than 0.3 g Zn) carefully added, and electrolysis effected without heat, by a current of $ND_{100} = 0.3–0.5$ amperes. The reaction is complete in 2 to 3 hours.

N. Eisenberg† obtained the following results by the above method:

Subst. taken.	Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.	Condition of Metal.
1.8312	0.4 -0.35	3.95–4.00	25 –26°	4 hr.	16.35 %	partly spongy
1.8312	0.40-0.35	4.15–4.25	28.5-30°	4 " 15 m.	16.01 "	spongy

Remark: (1) Rough dish; (2) Polished dish.

The agitation of the liquid by means of a stirring appliance is recommended for this method.

According to Jordis, zinc, when present in the form of sulphate, chloride or nitrate, may be separated from a lactic

* [Theory 16.29% Zn.] † Inaugural-Dissert. Heidelberg, 1895.

acid solution. The ease with which this method may be carried out appears from the directions of the author, which read as follows:* "2 g ammonium sulphate and 5–7 g ammonium lactate are added to the neutral solution containing not less than 0.3–0.5 g zinc, and it is acidified with a few drops of lactic acid. A stirring attachment is employed, and the solution is electrolyzed with a current of $ND_{100}=1.0–1.5$ amp. After 40–60 minutes the electrolyte is poured into a second dish and the separation completed in this. With a current of the above density this requires 20–25 minutes. A somewhat more concentrated solution of about 120–150 cc is advantageous.

"Since the lactic acid is but very slowly decomposed during the electrolysis, its regeneration resulting from the action of the sulphuric acid formed upon the ammonium lactate, the electrolyte remains acid until the end and requires no further attention."

MANGANESE.

LITERATURE:

Richè, Ann. d. Chim. et Phys., [5], **13**, 508.
Luckow, Zeit. f. anal. Chem., **19**, 17.
Schucht, *ibid.*, **22**, 493.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622.
Moore, Chem. News, **53**, 209.
Smith and Fränkel, Journ. Anal. Chem., **3**, 385;
Chem. News, **60**, 262.
Brand, Zeit. f. anal. Chem., **28**, 581.
Rüdorff, Zeit. f. angew. Chem., **15**, 6.
Classen, Ber. deutsch. chem. Ges., **27**, 2060.
Engels, Zeit. f. Elektrochemie, 1895–96, p. 413; 1896–97, p. 286.
Groeger, Zeit. f. angew. Chem., 1895, p. 253.

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* Zeit. f. Elektrochemie, 1895–96, p. 656

From the results of experience in the Aachen laboratory, none of the methods long in use are applicable for the direct quantitative determination of this metal as peroxide. It is generally assumed that the peroxide when dried at about 68° has the composition $MnO_2.H_2O$, an assumption which the author cannot confirm. If the attempt be made to convert the hydrated peroxide into anhydrous peroxide by prolonged drying at a higher temperature, a strongly hygroscopic substance results which rapidly increases in weight during the process of weighing. It is therefore necessary to convert the dried peroxide into mangano-manganic oxide by ignition, an operation conducted with ease and safety. After determining the necessary conditions for the separation of large quantities of lead peroxide, the author was induced to assume that manganese behaved similarly to lead. Investigation proved, however, that strong inorganic acids interfere with complete precipitation, and even make it impossible. Of the organic acids, acetic acid alone is suitable, although the precipitation of large quantities, even when roughened dishes are used, cannot be successfully carried out, since it is impossible to obtain firmly adhering precipitates.

As will be stated under lead, the separation of lead takes place from nitric acid solutions in the presence of other metals. The hope that manganese in the presence of iron might be separated and determined in an acetic acid solution has not been fulfilled. Innumerable experiments, conducted under the most varied conditions and with the most diverse substances, have given no satisfactory results. In view of the great importance which a method for the direct determination of manganese in the presence of iron, etc., would possess, this investigation will be continued.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: 50–70°.
Current density: ND_{100} = 0.3–0.35 amp.
Electrode tension: 4.3–4.9 volts.
Time: 3 hours.

EXPERIMENT.

Used about 0.5 g $MnSO_4.(NH_4)_2SO_4.6H_2O$, which was dissolved in about 75 cc water and electrolyzed after the addition of 25 cc acetic acid sp. g. 1.069 (20°).

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.	
0.3-0.3	4.4–4.9	50–68°	3 hr.	0.1035 g Mn_3O_4	14.94 %*
0.3-0.35	4.3–4.6	56–62°	3 "	0.1045 g Mn_3O_4	15.04 "

An equally rapid and complete separation was secured by Engels, as a result of investigations conducted in the Aachen laboratory. The method is as follows: 1–2 g of the manganese salt is dissolved in about 125 cc of water, and 10 g ammonium acetate and 1.5–2 g chrome alum are also added. The clear solution is then electrolyzed. Chlorides must not be present, since the evolution of chlorine interferes with the separation of the manganese. If they are present, the process is carried out according to the directions given under the separation of manganese and copper.

CONDITIONS OF EXPERIMENT.

Temperature of liquid: 80°.
Current density: ND_{100} = 0.6–1 amp.
Electrode tension: 2.8–4 volts.
Time: About $1\frac{1}{4}$ hours.
Note: Roughened dishes *must* be used.

* [Theory 14.07% Mn. Probably impure salt was used.—Trans.]

EXPERIMENT.

In the determinations given below, 10 g ammonium acetate and 1.5–2 g chrome alum were added to the solution.

$Mn(NH_4)_2(SO_4)_2.6H_2O$.	Current Density ND_{100}. Amp.	Electrode Tension, Volts.	Temp.	Time.	Found* Mn_3O_4. g.	Per cent.
1.1522 g	0.6–0.5	2.8–3.1	80°	$\frac{5}{4}$ hr.	0.2235	19.39
1.2554 "	0.6–0.5	2.8–3.1	80°	" "	0.2436	19.40
1.2994 "	0.6	3.	83°	" "	0.2520	19.39
1.8099 "	1.1	3.7–4.1	80°	" "	0.3513	19.40

In the determination of manganese in the salts of permanganic acid, the solution of the latter is decomposed, according to Engels, with 5 cc acetic acid and enough hydrogen peroxide to completely decolorize it. Since the presence of even small quantities of hydrogen peroxide prevents the separation and the firm adherence of the precipitate, the excess of hydrogen peroxide must be removed. This may be most easily accomplished by the addition of small quantities of chromic acid, until further addition no longer causes the evolution of gas; generally 0.3–0.5 g is sufficient.

EXPERIMENT.

50 cc of a potassium permanganate solution were decomposed with 5 cc acetic acid and 10 cc of a weak solution of hydrogen peroxide. The excess of H_2O_2 was removed with CrO_3.

	Current Density.	Tension.	Time.	Temp.	Mn_3O_4.
I.	1.5 amp.	2.8 volts	1 hr.	85°	0.1217 g
II.	1.65 "	3.15 "	1 "	85°	0.1220 "
III.	1.78 "	3.4 "	1 "	80°	0.1220 "

The current strength available varies between comparatively wide limits. Weak currents also give rapid and satisfactory results.

* [Theory 19.52% Mn_3O_4.]

EXPERIMENT.

Three dishes, each containing manganese sulphate solution, 10 g ammonium acetate and 1 g chrome alum, were connected in parallel, and the current from a thermopile passed through. The tension at the electrodes at the beginning of the electrolysis was 3.2 volts, the entire current strength 1.5 amp., so that each dish received about 0.4 amp. The manganese salt used contained 20.45% Mn_3O_4.

$Mn(NH_4)_2(SO_4)_2.6H_2O$, Gram.	Current Density ND_{100}, Amp.	Tension, Volts.	Temp.	Time.	Found.
1.1955	0.22	3.2	80°	2 hrs. 30 min.	20.45 %
0.9009	0.22	3.2	80°	2 " " "	20.44 "
1.2012	0.22	3.2	80°	2 " " "	20.40 "

Since manganese separates as peroxide from a cold solution to which ammonium acetate has been added, at 1.25 volts, and when warmed to 80° as low as 1–1.1 volts, the electrolysis may therefore be conducted with low electromotive forces. The constancy of the latter may be assured by connecting in shunt (page 73). The lower the tension, the longer the time required for the separation. With the maximum tension of 1.8 volts it takes from 4 to 5 hours. For the firm adherence of the precipitate a temperature of 80° is essential.

In those cases (i.e., in the presence of silver) where the chrome alum produces a precipitate in the solutions, it may be replaced by 10 cc of alcohol, which in general is not as efficient as the chrome alum for separating the manganese peroxide.

When alcohol is used, the electrolysis is conducted at a temperature of 75–80°, with a maximum tension of 2 volts, which gives a current density ND_{100} = about 0.15 amp. Time required for the electrolysis, about 5 hours.

ALUMINIUM, URANIUM, CHROMIUM, BERYLLIUM.

If a solution of aluminium ammonium oxalate containing ammonium oxalate in excess is submitted to the action of the electric current, the ammonium oxalate is changed into carbonate, and the aluminium separates as hydroxide. When the oxalate is decomposed, the solution is heated until there is only a faint odor of ammonia, the hydroxide filtered off, washed with water, and converted, by ignition, into Al_2O_3.

Uranium is acted on in the same way as aluminium.

Chromium ammonium oxalate is oxidized by the current with formation of ammonium chromate. To determine the chromic acid, the ammonium carbonate is decomposed by boiling, the solution acidified with acetic acid, and the chromic acid determined as lead or barium chromate.

When beryllium ammonium oxalate is subjected to electrolysis, the beryllium is kept in solution by the hydrogen ammonium carbonate produced, provided the solution is cold.

The behavior of aluminium, chromium, uranium, and beryllium can be made use of, as explained later, to separate them from each other and from all metals which separate from their double oxalates in the metallic state at the negative electrode.

COPPER.

LITERATURE:

Gibbs, Zeit. f. anal. Chem., **3**, 334.
Boisbaudran, Bull. d. l. Soc. Chim., 1867, p. 468.
Merriek, Amer. Chemist, **2**, 136.
Wrightson, Zeit. f. anal. Chem., **15**, 299.
Herpin, *ibid.*, **15**, 335.
Ohl, *ibid.*, **18**, 523.
Classen, Ber. deutsch. chem. Ges., **14**, 1622, 1627.

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Hampe, Berg- und Hüttenm. Ztg., **21**, 220; **25**, 113.
Richè, Zeit. f. anal. Chem., **21**, 116.
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Rüdorff, Ber. deutsch. chem. Ges., **21**, 3050;
Zeit. f. angew. Chem.,1892, p. 5.
Luckow, Zeit. f. anal. Chem., **8**, 23.
Warwick, Zeit. f. anorg. Chem., **1**, 285.
Smith, Am. Chem. Journ., **12**, 329.
Croasdale, Journ. of Anal. and Appl. Chem., **5**, 133.
Foote, Am. Chem. Journ., **6**, 333.
Meeker, Journ. of Anal. and Appl. Chem., **6**. 267.
Classen, Ber. deutsch. chem. Ges., **27**, 2060.
Heidenreich, *ibid.*, **29**, 1585.
Regelsberger, Zeit. f. angew. Chemie (1891), **16**, 473.
Oettel, Chemiker-Zeitung, 1894, p. 879.
Schweder, Berg- und Hüttenmann. Ztg., **36** (5) **11**, 21.

If copper be reduced from a solution containing an excess of ammonium oxalate, it is not always possible to obtain the metal in a compact form. For this reason the author, as long ago as 1888,* began experiments on the determination of this metal from a solution of the acid double oxalate. Further experiments in this direction have shown that coherent, bright red copper precipitates can be obtained when copper is reduced from such solutions at a temperature of about 80°. The solution containing the copper is treated with a cold-saturated solution of ammonium oxalate, heated as directed, and at first electrolyzed for a few minutes without the addition of oxalic acid. A cold-saturated oxalic acid solution is then run in from a burette. The method of procedure here is similar to that described under Zinc (page 147).

In the analysis of substances low in copper, the solution may be made acid at the start; in concentrated solutions, on the contrary, the electrolysis must be conducted in solutions

* Ber. deutsch. chem. Ges., **21**, 2898.

which are as nearly neutral as possible, since otherwise difficultly soluble oxalate of copper will separate out, owing to the free oxalic acid present. The end of the reaction is determined by testing with potassium ferrocyanide a small portion of the solution strongly acidified with hydrochloric acid. The precipitate must be washed without stopping the current. The metal is dried in an air-bath after treating with water and alcohol.

The precipitated copper has a bright red color, adheres firmly to the dish, and has little resemblance to the copper precipitated from nitric acid solutions (see below). The chief advantage of this method is the rapidity with which it may be conducted.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: 80°.

Current density: $ND_{100} = 0.5–1$ amp. Most favorable current density $ND_{100} = 1$ amp.

Electrode tension: 2.5–3.2 volts.

Time of electrolysis: 2 hours.

EXPERIMENT.*

Used 1 g copper sulphate, 4 g ammonium oxalate, 120 cc liquid.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.	Taken.
1.0 –0.8.	2.8–3.2	80°	2 hr.	0.2531 g	0.2529 g
0.45–0.35	2.5–2.8	80°	2½ "	0.2528 "	0.2529 "

Copper precipitate bright red.

As has been observed by Luckow, copper may also be precipitated from a solution to which nitric acid has been added.

* Separation of copper from a solution of the ammonium double oxalate in the presence of free oxalic acid.

The reduction of copper from a nitric acid solution depends upon the presence of a certain quantity of nitric acid and the absence of chlorides. To about 200 cc of solution, containing the copper as sulphate, 20 cc of nitric acid* (sp. g. = 1.21) are added and the liquid is subjected to electrolysis. The end of the reaction is determined with ammonia.

The presence of chlorides is to be avoided. In the presence of antimony, arsenic, mercury, silver, tin, and bismuth, traces of these metals come down with the copper; but iron, cobalt, nickel, cadmium, manganese, and zinc can be separated from copper by this method.

According to the researches of Schröder large quantities of iron are detrimental, since a secondary reaction may take place between the ferric salt formed and the precipitated copper, which causes the copper to redissolve.

Copper separates in a crystalline form from solutions warmed to 50–60°; it is nevertheless impossible to separate the last traces of copper at this temperature.

CONDITIONS OF EXPERIMENT.

Temperature of solution: 20–30°.

Current density: ND_{100}=0.5–1 amp. The latter only when no other metal than copper is present in the solution.

Electrode tension: 2.2–2.5 volts.

Time: 4–5 hours. Agitating the solution with a stirring attachment hastens the operation.

EXPERIMENT.

Used about 1 g copper sulphate and 5% by volume nitric acid. Entire volume of liquid 120 cc.

*Such a large quantity of nitric acid is required only when the separation of copper from other metals is to be carried out. If no other metal than copper is present in the solution, 2 or 3 per cent by volume of nitric acid is sufficient.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.	Taken.
1.1–1.0	2.2 –2.5	25–30°	5 hr.	0.2490 g Cu	0.2495 g Cu
1.0–0.95	2.25–2.3	30–32°	5 "	0.2505 " "	0.2510 " "

A solution containing free nitric acid may also be used for separating such metals as are not reduced in the presence of this acid, or which are set free at the positive electrode in the form of peroxides. In such cases, however, it must be kept in mind that the nitric acid is gradually converted into ammonia, on account of which, after the current has acted for some time, nitric acid must be occasionally added.

Copper may be separated from a solution containing ammonium oxalate or one containing free nitric acid, in the presence of small quantities of antimony and arsenic. If, however, the amounts of the latter are considerable, then, after continued action of the current, antimony and arsenic are deposited upon the copper, causing the negative electrode to appear more or less dark-colored. In order to determine the copper in such cases, the dried electrode is ignited for a short time, as a result of which the copper is oxidized and the antimony and arsenic are driven off. The residue of oxide is dissolved in nitric acid and again submitted to electrolysis.*

In general the presence of chlorides causes the copper to separate in a spongy condition. To avert this action and to secure an adherent precipitate, Rüdorff adds 2–3 g ammonium nitrate and 20 cc ammonia (sp. g. 0.96), dilutes with water to 100 cc, and electrolyzes this solution. At the close of the reduction the solution is acidified with dilute acetic acid, the dish filled to overflowing with water, emptied, shaken to remove the last drops of water, and dried at 100° in the air-bath.

In the laboratory of the Technical High School at Munich

* Mansfeld'sche Hüttendirection.

the preceding method is carried out under the following conditions: Ammonia is added in slight excess until the precipitate which at first appears is redissolved. Then 20–25 cc ammonia, sp. g. 0.96, are added, in case not more than 0.5 g copper is present.* In this solution 3–5 g ammonium nitrate are dissolved and the electrolysis is conducted with a current of $ND_{100} = 2$ amperes. The precipitate must be washed without interrupting the current.

Oettel, who also carried out experiments on the quantitative determination of copper from ammoniacal solutions, found that by the addition of ammonium nitrate 0.2–0.25 g of copper sulphate were quantitatively reduced in 6–8 hours at ordinary temperatures. The results of his investigation are:

"1. That copper can be separated in a compact form from weakly ammoniacal solutions containing ammonium nitrate, by currents of $ND_{100} = 0.07$–0.27 ampere. With too little ammonium nitrate, as well as in the presence of large quantities of free ammonia, the precipitate shows a tendency to a spongy structure.

"2. The highest concentration of the solution is 0.8 g copper per 100 sq. cm. electrode surface, with the employment of a wire-shaped positive electrode.

"3. The presence of chlorine, zinc, arsenic, and small quantities of antimony is without detrimental action; when the solution contains lead, bismuth, mercury, cadmium, or nickel, the results of the determinations are somewhat too high."

E. F. Smith† precipitates copper from a solution which contains sodium phosphate and free phosphoric acid. Heidenreich, who tested the method in the Aachen laboratory, obtained the following results.

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* If as much as 1 g Cu is present, the quantity of ammonia is increased to 30–35 cc.

† Electrochemical Analysis, p. 92.

EXPERIMENT.

100 cc of a solution of Na_2HPO_4 (1.0358 g) and 3.5 cc of a solution of phosphoric acid (1.347 g) were diluted with water to 110 cc. To this solution the copper solution was added.

Taken.	Volts.	Time.	Found.*
0.3959 g	2.4–2.6	17 hr.	25.41 %
0.3982 "	2.4–2.6	17 "	25.26 "

The copper separated at first brilliantly metallic, but as the electrolysis proceeded it became dark red and spongy. Variations of the conditions, such as increasing the tension, led to no better results. Owing to the spongy condition of the precipitate, the results came too high.

For the special determination of copper, in copper-aluminium alloys, Regelsberger suggests dissolving 3–5 g of the alloy in nitric acid and evaporating the solution down to the consistency of sirup. The sample is diluted, and a measured quantity (corresponding to 0.6–1 g substance) is poured into the electrolytic cell. An excellent precipitate is obtained if the acid solution is neutralized with ammonia and 10 cc of dilute nitric acid (sp. g. 1.2) are added to 200 cc of the liquid. The clear solution is electrolyzed with a current density $ND_{100} = 0.4$ amp. When the solution is warmed the separation is completed in about three hours.

A rapid and accurate method for the determination of copper has been worked out by Carl Engels in the Aachen laboratory. This method has the advantage over the use of nitric acid solutions that it can be more rapidly performed, and that, in separations, it also dispenses with the tedious conversion of the nitrates into sulphates. This method is based upon the addition of urea.

The separation of copper from solutions containing sul-

* [Theory 25.33% Cu.]

phuric acid is possible also if hydroxylamine be added. The method is as follows:

If the separation is to be carried out with weak currents, say during the night, the addition of 2 cc concentrated sulphuric acid and about ½ g hydroxylamine sulphate is recommended. A fine crystalline precipitate and absolutely accurate results are obtained with a current strength of $ND_{100} = 0.08–0.18$ ampere. The tension at the poles of a shunt circuit was 1.8–2.2 volts; after connecting the dish the tension sank to 1.1–1.3 volts, with a current of 0.1–0.2 amp.

EXPERIMENT.

Taken $CuSO_4.5H_2O$.	Current Density ND_{100}.	Tension, Volts.	Time.	Found. Cu.	Per cent *
1.0130 g.	0.1 amp.	1.1	Night	0.2574	25.41
1.7065 "	0.12 "	1.3	"	0.4335	25.40
1.1893 "	0.1 "	1.2	"	0.3021	25.41

If stronger currents are used, the amount of sulphuric acid must be increased. 10–15 cc of conc. sulphuric acid are poured into the solution of the salt, it is diluted to 150 cc, and 1 g hydroxylamine sulphate is added. If 0.3–0.5 g Cu is present, with a current strength of $ND_{100} = 1$ amp., the separation is finished in 1½ to 2 hours. The condition of the precipitated copper is much better and much more suited for quantitative determination than the copper obtained under similar conditions without the addition of hydroxylamine.

Urea exerts a far more satisfactory action than hydroxylamine upon the separation of copper from solutions containing sulphuric acid. With a current strength of $ND_{100} = 1$ ampere, not the slightest tendency toward a spongy separation is exhibited, but a bright-red crystalline coating is obtained on the negative electrode. The analysis, with the stated current density, is completed in 1¼ hours.

10–15 cc concentrated sulphuric acid and 1 g urea are

* [Theory 25.33% Cu.]

added to the solution of the copper, which is then diluted to 150 cc.

CONDITIONS OF EXPERIMENT.

Temperature of liquid: Most suitable, 60–70°.
Electrode tension: 2.7–3.1 volts.
Current density: $ND_{100} = 0.8$–1 amp.
Time: $1\frac{1}{4}$ hours.

EXPERIMENT.

Used $CuSO_4.5H_2O$.

Quant. subst., g.	Current Density ND_{100}, Amp.	Tension, Volts.	Temp.	Time.	Found.*
1.1364	1.05	3.1	25°	1 hr. 15 m.	25.09 %
0.9671	1.2	3.1	55°	1 " 15 "	25.09 "
1.3972	0.75	2.7	65°	1 " 45 "	25.09 "

The current may be interrupted in washing the precipitate. The separated copper contains traces of carbon, and also platinum which dissolves from the anode. These admixtures can be determined by dissolving the copper in dilute nitric acid (1 : 10). A thin dark coating remains on the dish, which may be washed with water, but not with alcohol, without becoming loosened. The weight of the dish, determined after washing and drying in the air-bath, is used as a basis for calculating the weight of the separated copper.

With weaker currents the length of time required is of course greater. With a current density of $ND_{100} = 0.2$ ampere, the precipitation of from 0.3 to 0.4 g Cu is completed in $3\frac{1}{2}$–4 hours. It is desirable in this case to add less sulphuric acid to the solution; 5 cc conc. H_2SO_4 to each 150 cc, is the proper proportion.

Four dishes were connected in parallel, and for every 150 cc of solution of the copper salt which they contained 1 g urea and 5 cc conc. H_2SO_4 were added. The four electroly-

* [Theory 25.33%.]

ses were then conducted in the cold, with the current from a thermopile. The entire current strength was $ND_{100} = 0.8$ ampere, so that each dish received a current of $ND_{100} = 0.2$ ampere. The analyses were completed in 4 hours. The per cent. of copper in the salt used was 25.08.

Used $CuSO_4.5H_2O$.	Found Cu.	Found %.
1.0101 g	0.2533 g	25.07
1.0815 "	0.2709 "	25.05
1.0320 "	0.2589 "	25.08
1.0111 "	0 2535 "	25.07

BISMUTH.

LITERATURE:

Luckow, Zeit. f. anal. Chem., **19**, 16.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622.
Thomas and Smith, Am. Chem. Journ., **5**, 114.
Moore, Chem. News, **53**, 209.
Smith and Knerr, Am. Chem. Journ., **8**, 206.
Schucht, Zeit. f. anal. Chem., **22**, 492.
Eliasberg, Ber. deutsch. chem. Ges., **19**, 326.
Brand, Zeit. f. anal. Chem., **28**, 596.
Vortmann, Ber. deutsch. chem. Ges., **24**, 2749.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 199.
Smith and Saltar, Zeit. f. anorg. Chem., **3**, 418.
Smith and Moyer, Journ. of the Am. Chem. Soc., **15**, 28, 101.
Smith and Knerr, Am. Chem. Journ., **8**, 206.
Schmucker, Zeit. f. anorg. Chem., **5**, 199.

Up to the present time it has been found impossible to quantitatively precipitate bismuth in a compact metallic form. It separates in a more or less spongy form from all its compounds. A discussion of the directions given by the different investigators will therefore be omitted.

G. Vortmann has attempted to separate bismuth as an amalgam. Since, however, the directions for the conditions of experiment are not given, the mere mention of this method will be sufficient.

CADMIUM.

LITERATURE:

Smith, Am. Phil. Soc. Pr., 1878.
Clarke, Zeit. f. anal. Chem., **18**, 104.
Beilstein and Jawein, Ber. deutsch. chem. Ges., **12**, 759.
Smith, Am. Chem. Journ., **2**, 43.
Luckow, Zeit. f. anal. Chem., **19**, 16.
Wrightson, *ibid.*, **15**, 303.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1628.
Warwick, Zeit. f. anorg. Chem., **1**, 258, 291.
Moore, Chem. News, **53**, 209.
Smith, Am. Chem. Journ., **12**, 329.
Vortmann, Ber. deutsch. chem. Ges., **24**, 2749.
Rüdorff, Ztschr. f. angew. Chem., 1892.
Classen, Ber. deutsch. chem. Ges., **27**, 2060.
Heidenreich, *ibid.*, **29**, 1586.

The separation* of this metal in a compact brilliant form has been shown, by experiments carried out at the Aachen laboratory, not to be possible by any of the methods hitherto described. It may be accomplished, however, by the electrolysis of a warm solution of the double oxalate which is kept acid with oxalic acid during the electrolysis. (A cold-saturated solution of oxalic acid is employed.) (See directions for Zinc.)

To prepare the double salt, the cadmium compound is dissolved in 20–25 cc water, by warming in a platinum dish; a hot solution, which should be previously filtered, of 10 g ammonium oxalate in 80–100 cc water is added and the solution is electrolyzed. As soon as the action of the current has begun, several cubic centimeters of oxalic acid are poured upon the watch-glass covering the dish, and the liquid is kept

*The metallic condition of the precipitated cadmium, all the conditions of the experiment being preserved, depends upon the absolute cleanliness of the surface of the cathode.

weakly acid during the electrolysis. The end of the reaction is determined with hydrogen sulphide, by testing a small portion of the solution acidified with hydrochloric acid. The metal must be washed without interrupting the current. (Method of the author.)

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: 70–75°.

Current density: $ND_{100} = 0.5–1$ amp.

Electrode tension: 3–3.4 volts.

Period of electrolysis: About 3 hours.

Maximum quantity of metal which can be precipitated: 0.15–0.16 g.

EXPERIMENT.

Used 0.3–0.4 g cadmium sulphate, 10 g ammonium oxalate, 120 cc liquid.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.	
0.6–0.5	2.75–3.4	72–76°	3 hr. 30 m.	0.1472 g	49.07 %*
1.0–0.8	3.0 –3.4	68–73°	3 "	0.1474 g	49.13 "

Precipitate brilliantly lustrous.

With regard to further experiments by this method and for data on the use of polished and roughened dishes, of which the former are in this case to be preferred, the dissertation of N. Eisenberg † should be consulted.

Smith and Luckow recommend the precipitation of cadmium from a solution of the chloride or sulphate, which has been saturated with sodium acetate. Eliasberg, who tested this method in the Aachen laboratory, found that the reduction took place readily when the solution, of about 100 cc volume, was treated with about 3 g sodium acetate and a few

* [The salt taken was probably $CdSO_4.H_2O$ containing 49.67% Cd.—Trans.]

† Eisenberg, Inaugural-Dissertation, Heidelberg, 1895

drops of acetic acid, and the electrolysis was carried out at a temperature of 40–50°.

In the laboratory of the Munich High School the foregoing method is practised as follows: The solution, neutralized if necessary, containing not more than 0.5 g cadmium, is treated with 3 g sodium acetate, and made weakly acid with acetic acid. The solution is warmed to 45°, and decomposed with a current of $ND_{100} = 0.02–0.07$ ampere. The metal is washed without interrupting the current, and quickly dried at 100°.

During the electrolysis the solution should *not* be warmed above 50°, on account of the formation of basic salts. Cadmium is only partly precipitated from solutions strongly acidified with acetic acid. By this method 0.2 g of cadmium may be separated in about five hours. The presence of nitrates is detrimental.

According to Beilstein and Jawein, the determination of cadmium may be conducted from a solution of the double salt with potassium cyanide. Aside from the fact that the necessary directions are not given, this method possesses no advantages, the precipitation of 0.2 g cadmium requiring about 12 hours.

Vortmann attempted the determination of cadmium by a method similar to that used for the determination of bismuth and zinc, by precipitation from a solution of the ammonium double salt in the form of amalgam.

E. F. Smith determines cadmium by dissolving the oxide in acetic acid, evaporating, taking up in water, and electrolyzing the solution thus obtained. Heidenreich, who carried out in the Aachen laboratory a series of varied researches on this subject, obtained no satisfactory results, either in the condition of the precipitate or in the quantitative separation of the metal.

A further method by E. Smith depends upon the reduction of cadmium from a solution to which sodium phosphate and free phosphoric acid have been added. Here also the quantitative separation of the cadmium does not take place, not even when the current is increased to 1 ampere.

Finally, Smith * has proposed a method for the separation of cadmium from a solution containing free acetic acid. According to the statements of Heidenreich, cadmium is precipitated from a solution containing 10 cc acetic acid (50%) to 120 cc of solution, by a current density of 0.4 ampere and a tension of 4.5 volts, in the form of small crystalline plates which cannot be washed without loss. Variations of the conditions of experiment (addition of less acetic acid [2–10 cc], employment of current densities of from 0.1 to 0.4 ampere and tensions of 4–7.5 volts, as well as different temperatures) gave no satisfactory results.

LEAD.

LITERATURE:

Kiliani, Berg- u. Hüttenm.-Zeitung, 1883, p. 253.
Luckow, Zeit. f. anal. Chem., **19**, 215.
Richè, Ann. d. Chim. et Phys., **13**, 508; Zeit. f. anal. Chem., **21**, 117.
Classen, Zeit. f. anal. Chem., **21**, 257.
Hampe, Zeit. f. anal. Chem., **13**, 183.
Parodi and Mascazzini, Ber. deutsch. chem. Ges., **10**, 1098;
Zeit. f. anal. Chem., **16**, 469; **18**, 588.
Richè, Zeit. f. anal. Chem,, **17**, 219.
Schucht, Zeit. f. anal. Chem., **21**, 488.
Tenny, Am. Chem. Journ., **5**, 413.
Smith, Am. Phil. Soc. Pr., **24**, 428.
Vortmann, Ber. deutsch. chem. Ges., **24**, 2749.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 198.

* Electrochemical Analysis, p. 95.

Warwick, Zeit. f. anorg. Chem., **1**, 258.
Classen, Ber. deutsch. chem. Ges., **27**, 163.
Kreichgauer, *ibid.*, **27**, 315; Zeit. f. anorg. Chem., **9**, 89.
Classen, Ber. deutsch. chem. Ges., **27**, 2060.
Medicus, *ibid.*, **25**, 2490.
Neumann, Chemiker-Zeitung, 1896, p. 381.

If a solution of a lead salt containing an excess of ammonium oxalate be electrolyzed warm, the lead separates at the negative electrode, adheres closely, and shows its characteristic metallic properties; but it oxidizes partially on washing with water and alcohol, so that the results are always too high. The precipitation of lead as amalgam presents some difficulties, inasmuch as some lead peroxide separates at the positive electrode and must be dissolved. According to G. Vortmann, the aqueous solution of the lead salt, containing sufficient mercuric chloride to produce the amalgam, is treated with 3–5 g sodium acetate and a few cubic centimeters of concentrated potassium nitrite solution. The precipitate produced by the latter reagent (which is added to prevent the formation of peroxide) is dissolved in acetic acid, and the clear yellow solution diluted and electrolyzed. If lead peroxide appears on the positive electrode during the reaction, more potassium nitrite is added. The close of the reaction is determined by testing with ammonium sulphide. As lead amalgam oxidizes rather readily when moist, it is quickly washed with water, alcohol, and ether, dried by the warmth of the hand and by blowing upon it, and finally in the desiccator.

The amalgam may also be separated from an aqueous solution acidified with nitric acid. However, as free nitric acid favors the formation of lead peroxide, more frequent addition of potassium nitrite is necessary, and complete precipitation is thereby seriously hindered.

In a solution containing free nitric acid, lead is acted on like manganese: it is oxidized, and separates as hydrated peroxide at the positive electrode. If there is no other metal in the solution, it must contain at least 10 per cent free nitric acid, according to Luckow; in the presence of other metals (mercury, copper, etc.), the oxidation is complete even in presence of little nitric acid.

In the Munich laboratory experiments have been conducted as to the quantity of nitric acid, sp. gr. 1.36, and have demonstrated that this depends on the temperature and the current density which is used. The current density depends in turn on the condition of the surface of the positive electrode. If this is very smooth, a current of $ND_{100} = 0.05$ is sufficient, otherwise one of $ND_{100} = 0.5$ is needed to produce an adherent precipitate. When $ND_{100} = 0.05$ ampere, 2 per cent by volume of nitric acid should be added when the solution is heated, and 10 per cent by volume at ordinary temperatures. When $ND_{100} = 0.5$ the volume-percentages are, respectively, 7 and 20 for heated and cool solutions.

Heating the solution to about 50° materially assists the separation. The precipitate may be washed without loss, after the current is interrupted.

Chlorine compounds must not be present in the solution for electrolysis.

Even when the stated conditions are observed, the quantity of lead which can be precipitated as peroxide in an adherent form is relatively small.* The rapid separation of large quantities of lead peroxide, firmly adherent like a metal, may only be carried out without difficulty, as the author's

* From experience in the Aachen laboratory, the greatest possible quantity is 0.15 g PbO_2 per 100 sq. cm. surface, while according to the statements of Dr. Cohen (Chem. Ztg., 1893, No. 98) as much as 0.3 g can be precipitated.

researches have shown, when the inside of the platinum dish serving as anode is roughened with a sand-blast.* By the use of such dishes, it is possible, with a current of 1.5 ampere, to precipitate in a few hours as much as 4 g of lead peroxide on 100 sq. cm. of surface.

For conducting the determination of lead, after the solution of the lead salt has been accomplished, 20 cc nitric acid (sp. g. 1.35–1.38) are added, the solution is diluted to about 100 cc, warmed to 60–65°, and electrolyzed with a current of $ND_{100} = 1.5–1.7$ amperes. If the warming is continued during the electrolysis, the precipitation of quantities up to 1.5 g lead peroxide is completed in about 3 hours; with larger quantities in about 4–5 hours. Complete precipitation is insured by adding about 20 cc of water and observing whether the freshly wetted surface of the electrode becomes darker. In case no blackening is observed at the end of 10–15 minutes, the current is stopped, and the precipitate is washed with water and alcohol, and dried at 180–190°. The residue is anhydrous peroxide.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: 60–65°.

Current density: $ND_{100} = 1.5–1.7$ amp.

Electrode tension: 2.5 volts. The tension is without influence upon the condition of the peroxide, and may vary within wide limits.

EXPERIMENT.

Used $Pb(NO_3)_2$ dissolved in 100 cc water, with the addition of 20 cc nitric acid (sp g. 1.35–1.38).

* The platinum refinery of G. Siebert in Hanau has faultlessly carried out the roughening in the desired manner at the request of the author. Such roughened dishes are of course applicable to all other electrolytic determinations.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.*
1.55–1.45	2.43–2.4	60–65°	1 hr. 5 m.	72.20 %
1.6 –1.58	2.48–2.43	60–65°	1 " 10 "	72.19 "
1.6 –1.65	2.41–2.36	60–65°	1 " 5 "	72.20 "

The preceding method permits of the separation of lead from zinc, iron, nickel, cobalt, manganese, copper, cadmium, gold, mercury, antimony, and aluminium; in the presence of silver and bismuth, traces of these metals in the form of peroxides pass over into the lead peroxide.

THALLIUM.

This metal may be completely precipitated from an ammonium oxalate solution.

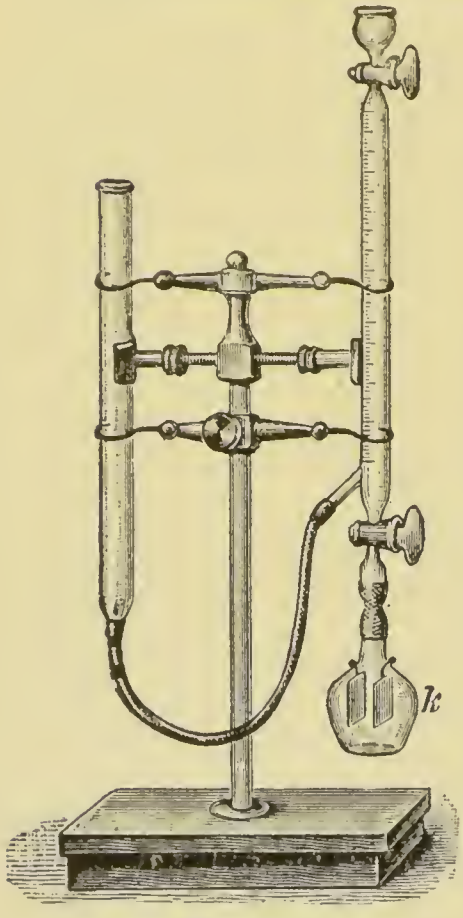

Fig. 85.

The properties of thallium, however, are similar to those of lead; its determination therefore requires special consideration.

G. Neumann, in connection with a research on certain double salts of thallium in the Aachen laboratory, has also investigated the quantitative determination of the metal. As his method is of value in the investigation of thallium compounds, it is here described. The process is based on precipitation of the thallium as metal, and determination of the volume of hydrogen set free by its solution in hydrochloric acid.

The apparatus shown in Fig. 85 is used for the process. K is a flask of about 100 cc

[* Theory 72.21% PbO_2.]

capacity, containing platinum-foil electrodes of 9 sq. cm. surface, terminating in contact-wires fused into the glass. The thallium salt and about 5 g ammonium oxalate are dissolved in this flask, and electrolyzed, after dilution, with a current of 0.1 ampere. The completion of the reaction is ascertained by testing with ammonium sulphide. As the

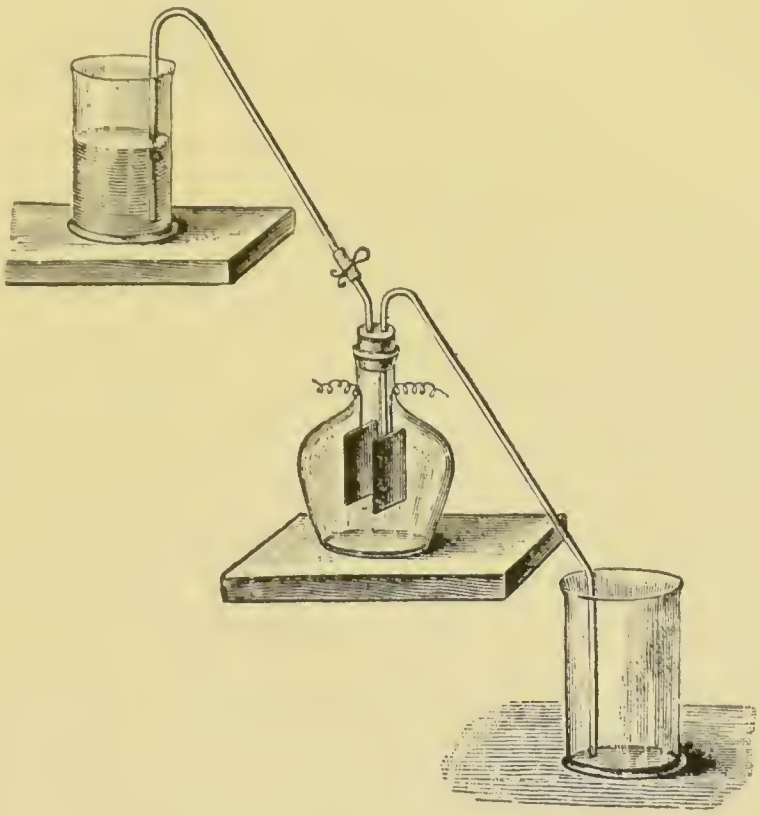

Fig. 86.

ammonium oxalate is converted into carbonate by the current, and the measuring-tube would be insufficient to contain the disengaged carbon dioxide, the solution remaining in the flask is removed after the reaction. This may readily be done by the use of two siphons. Neumann's automatic arrangement for this purpose is shown in Fig. 86; it is very convenient where many determinations are to be per-

formed, and its operation is easily seen from the figure. The washing is conducted without interrupting the current. To remove the gas-bubbles clinging to the electrode it is desirable to heat the flask a short time after the washing is complete. The flask is then connected to the measuring-tube, the thallium dissolved, and the hydrogen collected and measured in the usual way.

SILVER.

LITERATURE:

Luckow, Dingl. polyt. Journ., **178**, 43; Zeit. f. anal. Chem., **19**, 15.
Fresenius and Bergmann, Zeit. f. anal. Chem., **19**, 324.
Krutwig, Ber. deutsch. chem. Ges., **15**, 1267.
Schucht, Zeit. f. anal. Chem., **22**, 417.
Kinnicutt, Am. Chem. Journ., **4**, 22.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 5.
Eisenberg, Dissertation. Heidelberg, 1895.

Of the methods proposed for the determination of silver, the one suggested by Luckow (separation of the silver from the potassium double cyanide) is probably the most suitable. If insoluble silver compounds (silver chloride, silver oxalate) are to be analyzed, they are dissolved in potassium cyanide solution. For conducting the method, 3 g potassium cyanide are added to the solution, which is then diluted to 100–120 cc. Eisenberg, who tested the method in the Aachen laboratory, was convinced that the success of the same, as well as the metallic condition of the precipitated silver, depends upon the purity of the potassium cyanide used. Even the so-called "purissimum" potassium cyanide of commerce is unsuited. It is therefore desirable to prepare pure potassium cyanide by passing hydrocyanic acid gas into an alcoholic solution of potassium hydroxide.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: 20–30°.

Current density: $ND_{100} = 0.2–0.5$ amp.

Electrode tension: 3.7–4.8 volts.

Time of electrolysis: In the presence of equal quantities of silver, with current densities $ND_{100} = 0.2–0.5$ ampere, this varies from 5 to $1\frac{1}{2}$ hours.

For this determination, roughened dishes give best results.

EXPERIMENT.

(*a*) Experiment with the so-called "purissimum" potassium cyanide of commerce. Used silver sulphate.

Subst. taken.	Current Density, Amp.	Electrode Tension, Volts.	Temp.	Time.	Found.*	Condition of Metal.	Remark.
0.8660	0.4–0.2	3.35	22–24°	6 hr.	68.91%	Not firmly adherent	Rough dish.
0.8660	0.3–0.1	3.55	22–24°	6 "	68.91 "		Polished "

(*b*) Experiment with pure potassium cyanide. Used silver sulphate.

Subst. taken.	Current Density, Amp.	Electrode Tens., Volts.	Temp.	Time.	Found.	Condition of Metal.	Remark.
0.4369	0.3 –0.23	3.72	22°	5 hr.	69.08%	Firmly adherent	Roughened dish.
0.4370	0.52–0.54	4.6–4.8	20–30°	1 " 40 m.	69.00 "		
0.4369	0.32–0.21	3.70	22°	5 "	69.12 "	"	Polished dish.
0.8742	0.55–0.53	4.0	23°	2 " 40 "	68.98 "		

J. Krutwig treats the solution of the silver salt with ammonia in slight excess, adds ammonium sulphate, and electrolyzes.

In the Munich laboratory the following conditions have been determined for the preceding process. The solution, which must not contain more than 0.5 g silver, is treated

* [Theory 69.22% Ag.]

with 20 per cent by volume of ammonia (sp. gr. 0.96) and 5% ammonium sulphate solution (1 : 10), warmed, and electrolyzed with a current of $ND_{100} = 0.02 - 0.05$ ampere. After the current is stopped the precipitate must be very thoroughly washed to completely remove the ammonium sulphate.

Fresenius and Bergmann have found that silver can also be precipitated in a dense form from a solution containing nitric acid: 20 cc of nitric acid (sp. g. 1.2) are added to the silver solution, which is then diluted with water to about 200 cc and electrolyzed.

According to results in the Munich laboratory, it is desirable to add to the solution, which may contain as much as 0.4 g silver, 3 per cent by volume of nitric acid, sp. gr. 1.36, and to electrolyze the heated solution with a current of $ND_{100} =$ 0.04–0.05 ampere. The silver must be carefully washed without interrupting the current, to prevent loss. An insufficient quantity of nitric acid may lead to the formation of peroxide.

MERCURY.

LITERATURE:

Clarke, Am. Journ. of Sci. and Arts, **6**, 200.
Classen and Ludwig, Ber. deutsch. chem. Ges., **19**, 323.
Hoskinson, Am. Chem. Journ., **8**, 209.
Smith and Knerr, *ibid.*, **8**, 206.
Smith and Fränkel, Am. Chem. Journ., **11**, 264.
Smith, Journ. Anal. Chem., **5**, 202.
Vortmann, Ber. deutsch. chem. Ges., **24**, 2749.
Brandt, Zeit. f. angew. Chem., 1891, p. 202.
Rüdorff, *ibid.*, 1892, p. 5.
Eisenberg, Dissertation. Heidelberg, 1895.
Fränkel, Journ. Franklin Inst., **131**, 144.
Rising and Lenher, Berg- und Hüttenm. Ztg., **55**, 175.

The metal can be readily separated from solutions of the mercuric salts to which 4–5 g ammonium oxalate have been

added (method of the author). If the mercury is present as chloride in the solution, the electrolysis is continued until mercurous chloride disappears from the positive electrode.

CONDITIONS OF EXPERIMENT.

Temperature of liquid: Ordinary temperatures.
Current density: $ND_{100} = 0.1–1.0$ amp.
Electrode tension: 2.5–5.5 volts.
Time: Dependent on the current density.

Roughened dishes are preferable to polished, on account of the more uniform distribution and firmer adherence of the mercury to the cathode. On polished dishes the mercury separates in the form of small globules.

EXPERIMENT.

Subst. used. $HgCl_2$. g.	Current Density, Amperes.	Electrode Tension. Volts.	Temp.	Time. hrs.	m.	Found.* %	Remark.
0.4068	0.2 –0.15	2.6 –3.35	30–23°	5	15	73.74	
0.4073	1.02–0.93	4.05–4.75	29–37°	1	30	73.63	
0.4076	1.08–0.92	4.42–4.88	25–40°	2	5	73.77	Roughened Dish.
0.4080	1.15–1.09	4.97–5.05	18–40.5°	2	5	73.87	
0.4080	1.12–0.93	4.95–4.85	18–38°	2	5	73.84	
0.4080	1.52–0.48	3.65–4.65	16–27°	3	55	73.67	
0.4070	0.2 –0.23	2.89–3.75	28–24°	5	15	73.80	
0.4073	1.06–0.95	4.45–5.00	30–39.5°	1	30	73.29	
0.4076	1.16–1.09	5.32–5.53	23–40°	2	5	73.93	Polished Dish.
0.4080	1.20–0.99	4.70–4.90	18–43°	3	—	73.55	
0.4075	1.51–0.48	3.87–4.50	16–30°	3	55	73.85	

Mercury may also be quantitatively precipitated from a solution containing nitric, sulphuric, or hydrochloric acid. If no other metal than mercury is present, 1–2 per cent by volume of nitric acid is sufficient; while in the presence of other metals, which are not precipitated from solutions con-

* [Theory 73.85% Hg.]

taining free acid, 5 per cent by volume is required. In the latter case a current density not greater than 0.5 ampere is employed; in the former the current density may be raised to 1 ampere.

If hydrochloric acid is used, only a few drops are added, since larger quantities have a detrimental action on the separation of the metal. Large quantities of chlorides have an action similar to that of large quantities of hydrochloric acid.

Insoluble mercury compounds may be easily electrolyzed by suspending them in water slightly acidified with hydrochloric acid, or in a dilute solution of sodium chloride (about 10 per cent). This process, originated by the author, is used at Almadèn for determining the amount of mercury contained in cinnabar.

Edgar F. Smith precipitates mercury from the solution of the same in potassium cyanide. The solution of the mercuric salt, which may contain about 0.2 g mercury, is decomposed with 0.25–2 g potassium cyanide, diluted with water to 175 cc and electrolyzed.

Heidenreich, in the Aachen laboratory, determined the conditions of experiment for this method.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: Ordinary temperatures.
Current density: $ND_{100} = 0.03–0.08$.
Electrode tension: 1.65–1.75 volt.
Time: Dependent on the current density.

Taken.				Current Dens. ND_{100}, Amp.	Tension, Volts.	Time.	Found.*
0.2501 g	$HgCl_2$,	2–3 g	KCN	0.08–0.04	1.65–1.69	5 hr.	73.61% Hg
0.2655 "	"	"	"	0.03	1.75	14 "	73.50" "

The metal reduced by this method must be washed with water only, and not with alcohol, since, on washing with

*[Theory 73.85% Hg.]

the latter, small quantities of the mercury will become loosened and be carried away.

GOLD.

LITERATURE:

Luckow, Zeit. f. anal. Chem., **19**, 14.
Brugnatelli, Phil. Magazin, **21**, 187.
Smith and Muhr, Ber. deutsch. chem. Ges., **23**, 2175.
Smith and Wallace, Proceed. Chem. Soc. Franklin Inst., **3**, 20.
Smith, Am. Chem. Journ., **13**, 206.
Persoz, Annal. Chem. Pharm., **65**, 164.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 695.

Gold may be separated in a compact form from solutions of gold salts in potassium cyanide. To form the double cyanide, about 3 g of potassium cyanide are added. The solution is then electrolyzed at ordinary temperatures or at temperatures between 50° and 60°. Since the gold can be removed from the platinum dish with aqua regia only (an operation by which the platinum is also dissolved), platinum dishes coated with a thin deposit of silver have previously been used for this determination. According to a private communication from Dr. W. Dupré of Stassfurt, the gold may be readily removed from the platinum dishes by warming with a solution of chromic anhydride in saturated sodium chloride solution. The author can confirm this statement; in this operation gold only, and no platinum, goes into solution.

Since the conditions of experiment for the separation of gold from double cyanides had not been previously determined, they were ascertained by Dr. v. Wirkner at the suggestion of the author.

CONDITIONS OF EXPERIMENT.

Temperature of the liquid: Ordinary temperatures; or better 50–60°, since at ordinary temperatures a brownish decomposition product of potassium cyanide often separates.

Current density: $ND_{100} = 0.3–0.8$ amp.
Electrode tension: 2.7–4 volts.

EXPERIMENT.

A solution of chloride of gold of unknown strength was used. The electrolyses were carried out in roughened platinum-iridium dishes without a coating of silver. Used 3 g potassium cyanide, 120 cc liquid.

Taken, cc Gold Chloride Sol.	Current Density, Amperes.	Electrode Tension, Volts.	Temperature.	Time, hr.	m.	Found, g.
15	0.3	3.5–3.9	20–27°	5	—	0.0545
15	0.35	3.9–4.0	22–28°	14	(overnight)	0.0548
30	0.37	3.6–3.9	20–28°	4	15	0.1099
15	0.38	2.7–3.8	52–55°	1	30	0.0544
15	0.38	2.7–3.4	53–54°	1	20	0.0546
15	0.39	2.7–3.8	52–56°	1	30	0.0545
15	0.85	4.0–4.1	52–56°	1	30	0.0544

ANTIMONY.

LITERATURE:

Wrightson, Zeit. f. anal. Chem., **15**, 300.
Parodi and Mascazzini, *ibid.*, **18**, 588.
Luckow, *ibid.*, **19**, 13.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622; *ibid.*, **17**, 2467; **18**, 1104.
Leerenier, Chemiker Zeitung, **13**, 1219.
Vortmann, Ber. deutsch. chem. Ges., **24**, 2762.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 199.
Classen, Ber. deutsch. chem. Ges., **27**, 2060.

Antimony is precipitated from hydrochloric acid solution, but not in an adherent form. If potassium oxalate is added to the solution of the trichloride, antimony is easily reduced, but adheres even less closely than in the other case. An adherent metallic deposit can be obtained by adding potassium tartrate, but the separation is then too slow.

The precipitation of antimony from the solutions of its sulpho-salts is complete and satisfactory. If ammonium sulphide is used to produce a double salt, it must contain neither free ammonia nor polysulphides. Ammonium hydrosulphide, therefore, is convenient for the determination; it is kept in small, tightly corked bottles.

When a solution of antimony containing ammonium sulphide is electrolyzed, there is formed over the metal a coating of sulphur which cannot be washed off with water. When the metal is washed afterward with alcohol, the thin coating of sulphur can be removed by rubbing with the finger or a handkerchief moistened with alcohol, without danger of loss.

The use of ammonium sulphide has the disadvantage that, when several determinations are made together, the odor becomes unbearable. For this reason the author has made a series of experiments with potassium and sodium monosulphide and hydrosulphide, the results of which show that the precipitation of antimony from double salts with these compounds proceeds satisfactorily. As sodium sulphide (Na_2S) is the one of the salts named which is most desirable for facilitating the separation of antimony from tin and arsenic, the following particulars relate exclusively to the use of this salt * for the determination of antimony.

The following equations probably represent the reactions which take place in the electrolysis of the antimony sulpho-salt. The current first decomposes water:

$$3H_2O = 6H + 3O.$$

At the cathode:

$$Sb_2S_3 + 3Na_2S + 6H = 2Sb + 6NaHS.$$

At the anode:

$$6NaHS + 3O = 3Na_2S_2 + 3H_2O.$$

* For the preparation of this salt, see section on Reagents.

The reduction of antimony from the prepared sulpho-salts can be carried out as well at ordinary as at higher temperatures. In the first case the determination requires 17–18 hours, in the latter about 2 hours. If the separation is conducted in polished dishes, only relatively small quantities of the metal can be made to adhere firmly to the dish, and the employment of weak currents is necessary. In recent experiments roughened dishes have been used, and the reduction has been conducted from hot solutions and with stronger currents.

To carry out the analysis, 80–100 cc of a solution of sodium monosulphide (sp. g. about 1.14) are added to the antimony solution, which is diluted with water to 120 cc, and electrolyzed. If the metal is precipitated from a warm solution, it must be washed without interrupting the current. The end of the reaction can only be determined with certainty by the use of another electrode which is dipped into the liquid and brought into contact with the dish, i.e., the cathode.

The dish with the separated antimony is treated in the usual way with water and perfectly pure absolute alcohol, dried for a short time in the air-bath at 80–90°, and weighed.

CONDITIONS OF EXPERIMENT.

A. Temperature of the liquid: Ordinary temperatures.
Current density: $ND_{100} = 0.3–0.35$ ampere.
Electrode tension: 1–1.8 volts.
Remark: It is best to use roughened dishes only.

EXPERIMENT.

Used tartar emetic.*

Subst. taken, g.	Current Density, Amp.	Electrode Tension, Volts.	Time.	Found, %.	Condition of the Metal.
0.7892	0.35	1.70–1.06	17 hr. 30 m.	37.84	bright metallic, adherent.
0.7894	0.35	1.80–1.00	17 " 30 "	37.80	

* [Probably impure anhydrous, $KSbC_4H_4O_7$ containing about 37.12% Sb.—Trans.]

B. Temperature of the liquid: 55–70°.
Current density: $ND_{100} = 1.0–1.5$ amp.
Electrode tension: 1–2 volts.

Subst. taken, g.	Current Density, Amp.	Electrode Tension, Volts.	Temp.	Time. hr.	Time. m.	Found, %	Condition of the Metal.
0.7895	1.00–1.2	1.45–1.25	55–60°	2	5	37.64	bright metallic
0.7895	1.06–1.25	1.35	65–70°	2	15	37.57	
0.7898	1.50	1.42	70°	1	45	37.85	
1.5873	1.50	1.80	70–80°	2	30	37.84	

The method of determining antimony in solutions of the polysulphides of the alkalies is very simple. The solution containing polysulphides is treated with an excess of hydrogen peroxide and heated till it becomes colorless. If a great excess of hydrogen peroxide is used, it may happen that the alkali sulphide is entirely decomposed and antimony sulphide precipitated. If the solution is entirely colorless, or if a precipitate of antimony sulphide has already appeared, the solution is cooled, 80 cc of a solution of sodium monosulphide are added, the whole is diluted with water to about 120–150 cc. and electrolyzed as above directed.

[Chittenden and Blake* have applied the electrolytic method to the determination of very small quantities of antimony in a large amount of organic matter. In test experiments, 100 g of beef or liver were finely divided, a few cubic centimeters of a standard antimony solution added, the mixture *thoroughly* oxidized with hydrochloric acid and potassium chlorate, all free chlorine removed by heat, and the antimony precipitated by hydrogen sulphide. The precipitate containing, together with antimony sulphide, some sulphur and organic matter, was dissolved in cold sodium monosulphide, and directly submitted to the action of a current from four gravity cells of

* Trans. Conn. Acad. Arts and Sci., 7, 276.

moderate size. The electrolytic action was continued till all the organic matter and sulphur was oxidized (eighteen to forty-eight hours), and the deposited antimony washed without breaking the current. Results satisfactory, and much better than those obtained by any other process.

Chittenden and Blake also found that antimony in small quantities was deposited quantitatively from urine by acidifying with sulphuric acid (1 cc dilute H_2SO_4 to 25 cc urine), and submitting directly to electrolysis. The battery used was the same as before.—*Trans.*]

PLATINUM.

LITERATURE:

Luckow, Zeit. f. anal. Chem., **19**, 13.
Classen, Ber. deutsch. chem. Ges., **17**, 2467.
Smith, Am. Chem. Journ., **13**, 206.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 696.

The compounds of platinum are very readily decomposed by the electric current, the metal being precipitated. According to the determinations made by Dr. W. Göbbels in the Aachen laboratory, if a solution of a platinum salt containing 2–3 per cent by volume of sulphuric acid is used for the decomposition and is electrolyzed with a current of $ND_{100} = 0.1$–0.2 ampere, all the platinum separates in a short time in the form of platinum-black. If, however, a solution heated to 60–65° is electrolyzed with a current of $ND_{100} = 0.05$ amp. and 1.2 volts tension, the platinum separates quantitatively and in a very compact form. The reduced metal is so dense that it cannot be distinguished from hammered platinum.

If the quantity of platinum is about 0.4 g, the solution of the platinum salt, according to the practice in the Munich laboratory, is treated with 2 per cent by volume dilute sul-

phuric acid (1 : 5), heated, and electrolyzed with a current of $ND_{100} = 0.01 - 0.03$ ampere; the precipitation is complete in about 5 hours.

Iridium is not reduced from its solutions by a current of $ND_{100} = 0.05$ amp. and 1.2 volts tension: this property may be used for the quantitative separation of platinum from iridium (Classen).

PALLADIUM.

LITERATURE:

Wöhler, Lieb. Ann., **133**, 357.
Schucht, Zeit. f. anal. Chem., **22**, 242.
Smith and Knerr, Am. Chem. Journ., **12**, 252.
Smith, *ibid.*, **8**, 206; **14**, 435.

Palladium is determined in the same way as platinum. If a current of $ND_{100} = 0.05$ ampere, with a tension of 1.2 volts, is used for the reduction, the palladium is obtained in an excellent metallic condition.

TIN.

LITERATURE:

Luckow, Zeit. f. anal. Chem., **19**, 13.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622.
Gibbs, Chem. News, **42**, 291.
Classen, Ber. deutsch. chem. Ges., **17**, 2467; **18**, 1104.
Bongartz and Classen, *ibid.*, **21**, 2900.
Rüdorff, Zeit. f. angew. Chem., 1892, p. 196.
Classen, Ber. deutsch. chem. Ges., **27**, 2060.
Engels, Zeit. f. Elektrochemie, 1895–96, p. 418.
Freudenberg, Zeit. f. phys. Chem., **12**, 121.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1586.

Tin separates completely from a solution containing the ammonium double oxalate, or from an ammonium sulphide solution. Sodium and potassium sulphides cannot be used,

as tin separates only partially from a dilute solution of the corresponding sulpho-salt, and not at all from a concentrated solution.

If tin is precipitated from the ammonium double oxalate, a separation of stannic acid readily occurs, especially when much tin is present, which must be redissolved by addition of oxalic acid. The reduction of tin may be carried out without difficulty, however, if *acid* ammonium oxalate is used instead of the neutral oxalate. The results obtained by this process are so accurate that the author has found it adapted to the determination of the atomic weight of tin.*

The solution of tin is treated with a cold saturated solution of acid ammonium oxalate in the proportion of 20 cc to 0.1 g tin. The solution is diluted to about 150 cc and electrolyzed. The tin is completely precipitated as a closely adherent, shining, silver-white metal, even when as much as 6 g is present. The current is interrupted, and the metal washed as usual with water and alcohol, and dried at 80°–90°.

CONDITIONS OF EXPERIMENT.

Temperature of liquid : Ordinary temperatures.
Current density : $ND_{100} = 0.2–0.6$ amp.
Electrode tension : 2.7–3.8 volts.
Time of experiment : 8–10 hours.

EXPERIMENT.

Used 0.9–1 g $SnCl_4.2NH_4Cl$[32.10% Sn], 120 cc of a saturated solution of acid ammonium oxalate.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found.
0 2–0.3†	2.7–3.8	25°	8 hr. 5. m.	32.06%
0.3–0.6	2.8–3.8	30–35°	9 " 45 "	32.00"

* Bongartz and Classen, Ber. deutch. chem. Ges., **21**, 2900.
† Finally increased to 0.5 ampere.

If larger quantities of the tin salt are used, it is necessary to add acid ammonium oxalate from time to time, on account of the decomposition of the acid ammonium oxalate, which causes the solution to react alkaline. According to recent investigations, the determination of tin may be carried out by treating the solution of the tin salt with neutral ammonium oxalate to form the double salt, acidifying with oxalic acid and electrolyzing warm.

Heidenreich, who tested this method in the Aachen laboratory, found that the determination of tin can be completed in 4–4½ hours. 4 g ammonium oxalate to every 0.3 g tin present are added to the solution, which is then acidified with 9–10 g oxalic acid, warmed to 60–65°, and electrolyzed with a current of $ND_{100} = 1–1.5$ amperes. The precipitate must be washed without interrupting the current.

Instead of oxalic acid, acetic acid may be used; it possesses, however, no advantages. 100 cc of a saturated solution of ammonium oxalate are added to the solution of the tin salt, which is then acidified with 25 cc acetic acid (sp. g. 1.0615; about 50%). The metal is precipitated in the form of radiated crystals, in contrast to the precipitate from acid ammonium oxalate solutions. Tin adheres better to roughened than to polished dishes.

The following experiments were conducted by the acetic acid method:

Current Density, Ampere.	Electrode Tens., Volts.	Temp.	Time.	Found.
0.3 increased to 0.5	3.2–3.8	25°	6 hr. 15 m.	32.00%
0.5 " " 1.0	3.6–4.2	25–30°	5 " 45 "	32.01"

In these experiments the tin in the polished dishes appeared brilliantly crystalline, and in the roughened dishes silver-white.

Since tin, like zinc, is dissolved with difficulty from the

platinum dishes by acids, it is necessary to use fused acid potassium sulphate to remove it. It is therefore best to precipitate the tin in coppered dishes (see Zinc).

Engels worked out the following method in the Aachen laboratory: The tin salt is dissolved in water containing a few cubic centimeters of oxalic acid, and 0.3–0.5 g hydroxylamine, 2 g ammonium acetate, and 2 g tartaric acid are added for every 0.5–1.2 g tin salt taken. The solution is then diluted to 150 cc.

CONDITIONS OF EXPERIMENT.

Temperature of liquid: 60–70°.
Current density: $ND_{100} = 0.99$–1 amp.
Electrode tension: 4–5 volts.
Time: 3–5 hours.

EXPERIMENT.

$SnCl_4$. $2NH_4Cl$, g.	Current Density, Amp.	Electrode Tension, Volts.	Temp.	Time.	Found, g.	Found, Per cent.	Calculated.
0.9175	1–0.8	5.2–5.6	70°	3 hr.	0.2970	32.37	32.37%
0.9859	1–0.8	4.8–5.3	63°	3 "	0.3195	32.40	"
0.9050	1–0.9	5.0–5.6	65°	3 "	0.2931	32.39	"
1.1879	0.5	5.1–6.0	45°	6 "	0.3847	32.38	"
1.0026	0.7	3.4	60°	3 "	0.3238	32.36	"
0.9940	0.7	4.0	60°	3½ "	0.3219	32.38	"
1.0024	0.8	4.6	60°	3 "	0.3250	32.42	"
1.0022	0.8	4.2–4.4	60°	3 "	0.3252	32.44	"

In the solution of the ammonium sulpho-salt tin behaves like antimony. The tin solution (if necessary after neutralization with ammonia) is treated with ammonium sulphide free from ammonia (no more is added than is needed to form the sulpho-salt), diluted to 150–175 cc, warmed to 50–60°, and electrolyzed with a current of 1–2 amperes, at a tension of 3.5–4 volts. Under these conditions 0.3–0.4 g of tin can be reduced in an hour. Sometimes a deposit of sulphur adheres so strongly to the tin at the edge of the dish that it cannot be

washed off with water; it may, however, be easily removed, after washing with alcohol, by gentle rubbing with a linen cloth.

In gravimetric analysis tin is often separated from other metals by sodium sulphide instead of ammonium sulphide. In order to determine the tin electrolytically in such cases, the sodium sulphide must be converted into ammonium sulphide.* To accomplish this, the solution is treated with about 25 g pure ammonium sulphate free from iron, and heated very carefully, with the dish covered, till the hydrogen sulphide has all escaped; the solution is then kept in gentle ebullition for about fifteen minutes. Complete conversion into ammonium sulphide is shown by the greenish-yellow color of the solution. If the heating is continued too long, tin sulphide may separate; it can be dissolved in ammonium sulphide. After it is completely cooled, any sodium sulphate that may have separated is dissolved by addition of water, and the solution electrolyzed.

The determination of the tin is much more simply and easily accomplished by converting the solution of tin sulphide in sodium sulphide into the acid oxalate. This conversion may be accomplished in two ways; either the sulpho-salt is decomposed with dilute sulphuric acid to remove the greater part of the sulphur as hydrogen sulphide, and the separated tin sulphide oxidized with hydrogen peroxide † until the stannic acid which is produced appears clear white, or the heated alkaline solution is treated directly with hydrogen peroxide (of which a great quantity is needed), then acidified with sulphuric acid to precipitate stannic acid, neutralized with

* Sodium sulphide cannot be replaced by potassium sulphide in the separation from other metals, because the latter produces difficultly soluble potassium sulphate when ammonium sulphide is formed.

† Classen and Bauer, Ber. d. ch. Ges., 16, 1062.

ammonia, and treated with more hydrogen peroxide. In either case the solution is heated to decompose the excess of hydrogen peroxide, and the stannic acid allowed to settle and then filtered off. The precipitate is washed with the oxalate solution from the filter into a beaker, the filter washed with hot oxalic acid solution, and the stannic acid in the beaker dissolved by heating. Sometimes there is a residue of sulphur, which is removed by filtration. The filtrate is collected in the weighed platinum dish to be used for the electrolysis, and the sulphur is washed with a cold saturated solution of ammonium oxalate or acid ammonium oxalate. The solution for electrolysis must contain at least 4 g of the oxalate.

ARSENIC.

LITERATURE:

Luckow, Zeit. f. anal. Chem., **19**, 14.
Classen and v. Reiss, Ber. deutsch. chem. Ges., **14**, 1622.
Moore, Chem. News, **53**, 209.
Vortmann, Ber. deutsch. chem. Ges., **24**, 2764.

Arsenic cannot be quantitatively separated either from aqueous solutions or from solutions containing hydrochloric acid, ammonium oxalate, or alkali sulphides. From aqueous as from oxalic acid solutions a part of the metal is reduced, while from hydrochloric acid solutions, if the current is allowed to act for a sufficient length of time, all of the arsenic passes off in the form of arseniuretted hydrogen.

The behavior of arsenic (present as arsenic acid) in a concentrated solution of sodium sulphide permits the separation of arsenic from antimony, as will be shown later.

POTASSIUM, AMMONIUM. (NITROGEN.)

Potassium and ammonium may be determined, as is well known, by converting them into potassium or ammonium platinchloride, and weighing the precipitate, dried at 110°, on a tared filter. This method, which is almost universally em-

ployed in the separation of potassium from sodium, has many disadvantages. It is preferable, after precipitating and washing the platinum salt as usual, to dissolve it in water, and determine the platinum as directed on p. 182.

DETERMINATION OF NITRIC ACID IN NITRATES.

As is well known, nitric acid is often converted into ammonia, and the latter determined. The action of the galvanic current converts nitric acid into ammonia, as explained in the Introduction (p. 3). If the solution of an alkali nitrate, acidified with dilute sulphuric acid, is exposed to the action of the galvanic current, no ammonia is formed.

Luckow discovered that reduction of the nitric acid always takes place when a salt from which the metal is precipitated by the current is also present in the solution. Copper salts are best adapted for this purpose. G. Vortmann has determined in the Aachen laboratory the conditions for the quantitative determination of nitric acid in nitrates. The solution of the nitrate is treated with a sufficient quantity of copper sulphate (in the analysis of potassium nitrate, e.g., half as much crystallized copper sulphate as potassium nitrate), acidified with dilute sulphuric acid, and electrolyzed cold. When the reaction is complete the solution is poured off, sodium hydroxide solution is added, and the ammonia distilled off and determined volumetrically in the usual way. For this purpose one-fifth normal solutions of ammonia and sulphuric acid are used. To standardize the sulphuric acid, a weighed quantity (0.5 g) of crystallized copper sulphate is decomposed electrolytically, and the resulting free acid titrated with ammonia. G. Vortmann decomposed 0.4876 g $CuSO_4.5H_2O$, and used, for the neutralization of the acid set free, 19.6 cc of ammonia of a strength equal to the one-fifth normal sulphuric acid. 1 cc of the latter corresponds therefore to 0.0028017 g of nitrogen in the form of ammonia.

DETERMINATION OF THE HALOGENS.

Chlorine, Bromine, Iodine.

LITERATURE:

Vortmann, Monatshefte f. Chem., **15**, 280; **16**, 674;
Elektrochem. Zeit., 1894 (1), p. 137.

The method originated by Vortmann depends upon the principle that the halogens are set free from solutions of halogen salts by the electric current, and while in the ion state combine with a silver anode to form insoluble silver halide. The increase in weight of the anode gives directly the quantity of halogen which has separated. The completion of the analysis is determined by replacing the original silver anode by a second weighed silver anode and noting its increase in weight.

For an experimental test of the method, a weighed quantity of iodide is dissolved in water, 6–10 cc of a 10% solution of sodium hydroxide added, and the solution diluted to 100–150 cc. The silver anode, having the form of a watch-glass 6 cm. in diameter, is fixed about 5 mm. from the bottom of the copper dish which serves as cathode.

The cold solution is electrolyzed with a current strength of 0.03–0.07 ampere and a tension of 2 volts. After 4–5 hours the greater part of the iodine has been converted into silver iodide, and the remainder may be separated on a fresh silver anode, after the addition to the solution of sodium potassium tartrate. The liquid is warmed to 50–70° and electrolyzed with a current having a tension of 1.2–1.3 volts and a current strength of 0.01–0.02 ampere.

SEPARATION OF METALS.

IRON.

Iron—Cobalt.

LITERATURE.

Classen, Ber. deutsch. chem. Ges., 27, 2060.

The two metals may be determined by electrolyzing the solution of the double oxalates, as directed under Iron (p. 138), weighing the iron and cobalt together, and determining the former volumetrically.

After weighing the iron and cobalt, the deposit is dissolved in dilute sulphuric acid (dilute sulphuric acid is poured over the metals, and concentrated acid gradually added, so that the solution becomes heated), and the iron is titrated in the platinum dish with potassium permanganate. To overcome the red color of cobalt sulphate, a sufficient amount of nickel sulphate is added before the titration. The end of the reaction is easily recognized.

The residue of cobalt and iron may also be dissolved in hydrochloric acid, the iron oxidized with hydrogen peroxide, and titrated with stannous chloride, after removing the excess of hydrogen peroxide by boiling.

EXPERIMENT.

Used 1 g each of $CoSO_4.K_2SO_4.6H_2O$ and $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$, and 8 g ammonium oxalate. Volume of liquid, 120 cc.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time.	Found, Fe + Co.	Calculated.	Titrated.
2.0–1.6	3.0–3.6	65–70°	1 hr. 40 m.	0.2658 g	0.1141 g Fe* 0.1517 " Co 0.2658 g	0.1140 g Fe
1.55–1.4	3.2–3.6	62–65°	1 " 20 "	0.2650 "	0.1138 g Fe 0.1517 " Co 0.2655 g	0.1140 " "
1.0–0.85	2.85–3.1	60–65°	2 " 30 "	0.2585 "	0.1137 g Fe 0.1451 " Co 0.2586 g	0.1140 " "
0.5–0.4	2.0–2.7	60–67°	4 " —	0.2593 "	0.1136 g Fe 0.1452 " Co 0.2588 g	0.1133 " "
0.5–0.45	2.35–2.7	58–62°	4 " —	0.2617 "	0.1139 g Fe 0.1477 " Co 0.2616 g	0.1141 " "

Iron—Nickel.

LITERATURE:

Vortmann, Monatshefte f. Chem., **14**, 536.
Classen, Ber. deutsch. chem. Ges., **27**, 2060.

The method of determination is exactly like the preceding. Iron and nickel separate in the form of a beautiful white alloy scarcely distinguishable from the platinum. This alloy resists strongly the action of acids, and is only very slowly attacked by dilute sulphuric or hydrochloric acid.

Since the precipitation of the last trace of nickel takes place very slowly, the use of a current of at least $ND_{100} = 1$ ampere is to be recommended. Toward the end of the operation the current strength should be increased to 1 ampere.

To determine the iron, the precipitate in the dish must be heated with concentrated hydrochloric acid; and if the iron is to be titrated with permanganate, the solution must be

* The numbers placed under the heading " Calculated " are the quantities of iron and cobalt in the two salts taken, which were separately determined by electrolysis.

reduced by nascent hydrogen. It is more simple to oxidize with hydrogen peroxide, and, after removing the excess, titrate the ferric chloride with stannous chloride.

EXPERIMENT.

Used 1 g each of $NiSO_4.(NH_4)_2SO_4.6H_2O$ and $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$, and 8 g ammonium oxalate. Volume of liquid, 120 cc.

Current Dens., Amperes.	Electrode Tens., Volts.	Temp.	Time, hr. m.	Found, Fe + Ni.	Calculated.
2.2–1.75	3.45–4.0	70–65°	2 —	0.2760 g	0.1135 g Fe* 0.1622 " Ni 0.2757 g
2.0–1.75	3.35–3.9	69–67°	2 —	0.2654 "	0.1135 g Fe 0.1527 " Ni 0.2662 g
1.1–0.7	2.6–3.1	65–71°	4 30	0.2675 "	0.1135 g Fe 0.1550 " Ni 0.2683 g
0.5–0.4	2.6–3.0	68–71°	5 —	0.2664 "	0.2664 g

Vortmann adds 4–6 g sodium potassium tartrate and an excess of sodium hydroxide to the solution, and precipitates the iron with a current of $ND_{100} = 0.3–0.5$ ampere in three to four hours, the nickel remaining in solution.

Iron—Zinc.

LITERATURE:

Vortmann, Monatshefte f. Chem., **14**, 536.

If the double oxalates of iron and zinc are submitted to electrolysis, an alloy of the two does not separate, but zinc, with a little iron, is first precipitated on the negative electrode. The electrolysis proceeds very satisfactorily, and the

* The numbers placed under the heading "Calculated" are the quantities of iron and cobalt in the two salts taken, which were separately determined by electrolysis.

united weight of the two metals may readily be determined if there is less than one-third as much zinc as iron in the solution. If the proportion of zinc is greater, the zinc dissolves with the evolution of gas as the action proceeds, and a precipitate of iron oxide is formed.

Vortmann proposes the following method: Several grams of potassium sodium tartrate and an excess of a 10–20% solution of sodium hydroxide are added to the solution of the metals, and the liquid is electrolyzed at an electrode tension of 2 volts, with a current strength of $ND_{100} = 0.07–0.1$ ampere. It is best to raise the temperature at the close of the operation to 50–60°. After several hours the iron will be precipitated, the zinc remaining in solution.

Iron—Manganese.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **18**, 1787.

A solution of ammonium oxalate is decomposed by electrolysis, as stated in the introduction, mainly into hydrogen and hydrogen ammonium carbonate. The latter is partly decomposed into ammonia, most of which remains in solution, and carbon dioxide. In the electrolysis of a *hot* solution of ammonium oxalate, the ammonium carbonate produced by the current is partly neutralized as a result of dissociation of ammonium oxalate; carbon dioxide is rapidly liberated at the positive electrode.

If a solution of the double oxalates of iron and manganese is subjected to electrolysis without the previous addition of a great excess of ammonium oxalate, the characteristic color of permanganic acid appears immediately at the positive electrode, manganese dioxide gradually separates at the positive electrode, and iron at the negative. If the electrolysis is conducted under these conditions, it is impossible to obtain

a quantitative separation of the two metals, since the manganese dioxide carries down with it considerable quantities of ferric hydroxide. The complete separation of the metals is possible only when the separation of the manganese dioxide is delayed till most of the iron is precipitated. If a solution of the double oxalates of iron and manganese, which contains a great excess of ammonium oxalate, is electrolyzed *in the cold*, the greater part of the manganese dioxide is precipitated only after most of the ammonium oxalate is decomposed. In this case, however, the separation of the manganese dioxide is incomplete, because by the action of the current a considerable quantity of ammonium carbonate or ammonia is produced which acts on the manganese double salt, causing a portion of the precipitate (a mixture of dioxide and a lower oxide) to pass into solution.

The rapid dissociation of ammonium oxalate when heated gives a simple means of delaying, or entirely preventing, the formation of a manganese precipitate during electrolysis.

The double oxalate is prepared by the method given under iron, with the difference only that 8 to 10 g ammonium oxalate are dissolved in the liquid, which is warmed to 70°, and electrolyzed with a current of $ND_{100} = 0.5$ amp.

When the reduction is complete, the solution is poured off, the dish washed repeatedly with water, and this, together with traces of the dioxide precipitate, removed by alcohol; it is sometimes necessary to rub the dish gently with the finger.

The preceding method gives satisfactory results when the percentage of manganese is not too high. For the analysis of manganiferous iron (ferro-manganese, for example) this method has no practical value, since the per cent of manganese is here required, while by this method the iron is determined directly and the manganese must be determined in the liquid from which the iron has been separated.

To obtain a complete separation, the solution, containing suspended manganese dioxide, is heated with a solution of pure potassium or sodium hydroxide in a porcelain dish, till the ammonium carbonate produced by electrolysis is decomposed and the solution no longer has the odor of ammonia; and then sodium carbonate and a *small* quantity of sodium hypochlorite, or, better, hydrogen peroxide, are added. The manganese dioxide quickly falls to the bottom, and can be filtered off. The precipitate is best washed with hot water to which a little ammonium nitrate has been added, and is either converted into mangano-manganic oxide (Mn_3O_4) by ignition, or, better, into manganese sulphate ($MnSO_4$).

The conversion into manganese sulphate is accomplished by moistening the precipitate in the crucible with a little pure concentrated sulphuric acid, and igniting very gently, so that the bottom of the crucible is barely red.

If it is desired to determine the manganese as manganese sulphide, the solution is boiled till the ammonium carbonate is decomposed, the remaining ammonia is neutralized with nitric acid, and ammonium sulphide added till the precipitation is complete. The manganese sulphide is either determined as such, by ignition in a stream of hydrogen, or, more simply, converted into manganese sulphate by heating with a few drops of sulphuric acid.

Iron—Aluminium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **18**, 1795; **27**, 2060.

When a solution containing the above-named metals and a great excess of ammonium oxalate is electrolyzed *in the cold*, iron is deposited on the negative electrode, while the aluminium remains in solution as long as ammonium oxalate is present in the solution in greater proportion than the ammo-

nium carbonate formed from it. If a precipitate of aluminium hydroxide finally appears, it is only when the solution is almost free from iron. A small portion withdrawn by a capillary tube is tested, from time to time, with ammonium sulphide or another reagent already mentioned, and the current is stopped as soon as no reaction is obtained.

The process is as follows: The aqueous or weakly acid solution (in the latter case neutralized with ammonia) of the sulphates (the chlorides are not as well adapted to the process) is treated with ammonium oxalate in excess; and enough solid ammonium oxalate added (with gentle warming if necessary) to give the proportion of 2–3 g ammonium oxalate to 0.1 g of the metals. The entire volume of the solution should be 150–175 cc. If the temperature of the solution is not over 40°, it may be submitted to electrolysis at once, since it gradually cools under the action of a current of the given strength.

It is not best to continue the action of the current longer than is necessary to reduce the iron; for, otherwise, a large part of the aluminium is precipitated as hydroxide, and clings so closely to the negative electrode that it cannot be removed.

In such a case it is necessary to bring the aluminium hydroxide into solution by acidifying with oxalic acid, and, in case too much acid has been added, to pass the current till the last traces of the redissolved iron have been again precipitated.

The oxalic acid is poured gradually down the glass which covers the platinum dish, without interrupting the current, till there is no more ebullition, and the aluminium precipitate is dissolved.

If the quantity of the aluminium is not greater than that of the iron, the method gives good results without further treatment. In other cases, the precipitate of aluminium hydroxide is dissolved, without interrupting the current, by careful

addition of oxalic acid, and the electrolysis repeated until the iron is completely precipitated. To determine the aluminium in the solution poured off from the iron, it is heated in a porcelain dish till the ammonia is driven off, filtered, and the aluminium hydroxide converted, by ignition, into Al_2O_3.

EXPERIMENT.

Used 1 g each of $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$ and $Al_2(SO_4)_3.K_2SO_4.24H_2O$, and 8 g ammonium oxalate. Volume of liquid, 120 cc.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time hr. m.	Found, g.	Taken, g.
1.95–1.6	4 3 –4.4	31–42°	2 35	0.1143 Fe	0.1135 Fe
1.65–1.35	3.8 –4.1	30–48°	3 —	0.1159 "	0.1150 "
1.00–0.84	3.55–3.8	31–36°	4 30	0.1138 "	0.1135 "
0.50–0.42	2.75–3.1	30–32°	5 40	0.1139 "	0.1135 "

In order to avoid the separation of aluminium hydroxide (small quantities of which often adhere to the iron) strong currents, which raise the temperature of the solution, should not be used.

The effect of strong currents and high temperatures is illustrated in the above experiment.

Iron—Uranium.

The separation of iron from uranium depends upon the same principle as the separation from aluminium. It is necessary to have a great excess (8 g) of ammonium oxalate present in the solution, in order to retain the uranium in the form of the double salt until all of the other metals are reduced. The process is conducted in the same manner as in the separation of aluminium from iron. When a strong current is employed, especially when there is an insufficient quantity of ammonium oxalate present, it may happen that, as a result of

the decomposition of the hydrogen ammonium carbonate by the heat produced, the uranium is precipitated as hydroxide.

The uranium solution, after the other metals have been separated, is freed from oxalic acid by further electrolysis, and finally the ammonium carbonate is decomposed by heating.

To bring the finely divided precipitate of uranium hydroxide into suitable condition for filtration, nitric acid is added, the solution is heated till the precipitate is wholly dissolved, and ammonia is added to reprecipitate the hydroxide. The precipitate is converted into uranium oxide by ignition in a stream of hydrogen.

Iron—Chromium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., 27, 2060.

If a solution which contains an excess of ammonium oxalate, and chromium as sesquioxide, that is, as chromium ammonium oxalate, be submitted to electrolysis, all of the chromium is converted into a chromate. If iron is also present, it is precipitated in the metallic state on the negative electrode; the metal has a peculiarly characteristic lustre.

When the precipitation is complete, the liquid is poured off from the precipitated metal and is boiled to decompose ammonium carbonate, and the chromic acid reduced by boiling with hydrochloric acid and alcohol. The chromium is then precipitated as hydroxide with ammonia.

The hydroxide is converted into Cr_2O_3 in the usual manner, and weighed.

EXPERIMENT.

A. Used 1 g each of $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$ and $3K_2C_2O_4.Cr_2(C_2O_4)_3.6H_2O$, and 8 g ammonium oxalate. Solution diluted to 120 cc.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time, hr. m.	Found Fe.	Taken Fe.
2.00–1.60	3.4–3.6	62–68°	4 —	0.1123 g	0.1120 g
1.60–0.95	3.2–3.8	66–68°	5 —	0.1135 "	0.1135 "
1.95–1.50	3.3–3.7	62–65°	3 —	0.1130 "	0.1135 "

B. Used 2 g chrome alum, 1.5890 g ferrous ammonium sulphate, and 8 g ammonium oxalate.

1.5	3	65°	4	14.19% Fe	14.28% Fe

C. Used 2 g chrome alum, 1 g $Fe_2(C_2O_4)_3.3K_2C_2O_4.6H_2O$, and 8 g ammonium oxalate.

1.50–1.60	3.0–3.2	65°	4	11.35% Fe	11.40% Fe

Iron—Aluminium—Chromium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **14**, 2771.

The separation is performed as above. To separate the aluminium from chromium, the solution poured off from the precipitated metals is boiled till it has only a weak odor of ammonia, the aluminium hydroxide filtered off, and the chromium precipitated as above.

Iron—Chromium—Uranium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges, **14**, 2771; **17**, 2483.

The separation is accomplished by the precipitation of iron as metal, from the double oxalate solution, and the oxidation of chromium to chromic acid by the current. Uranium is separated as hydroxide, while chromium remains in solution as ammonium chromate. To accomplish the quantitative separation of chromium from uranium, the electrolysis must be continued till the oxalic acid is completely oxidized.

The solution is boiled to decompose the resulting ammonium carbonate, and allowed to stand six hours. The chromium is determined, as above, in the filtrate from the uranium.

Iron—Beryllium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **14**, 2771.

The separation of these two metals offers no difficulties whatever if the soluble double salts with ammonium oxalate are prepared, and if care is taken to have an excess of ammonium oxalate present. The iron is precipitated according to the directions given under the separation of aluminium from iron.

Strong currents are not advisable lest the solution become heated, and thus the ammonium carbonate, which holds the beryllium in solution, be decomposed. The beryllium hydroxide may, in any case, begin to precipitate before the iron is fully deposited. The determination of beryllium in the solution poured off from the iron is very simple; the solution is boiled to decompose the hydrogen ammonium carbonate, and the heating continued till the solution has only a weak odor of ammonia. The beryllium hydroxide is filtered, washed with hot water, and converted into BeO by ignition in a platinum crucible.

Iron—Beryllium—Aluminium.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **14**, 2771.

The process is precisely like the foregoing. When the iron is reduced, the solution is poured into a second platinum dish, and the action of the current is continued till all the

oxalic acid is decomposed, and the aluminium is precipitated as hydroxide. The beryllium is precipitated from the filtrate as hydroxide by boiling.

It is advisable to redissolve the aluminium hydroxide, to convert it again into the double oxalate, and to repeat the electrolysis.

Iron—Copper.

LITERATURE:

Vortmann, Monatshefte f. Chem., **14**, 536.
Classen, Ber. deutsch. chem Ges., **27**, 2060.

The separation may be accomplished according to the method given by Luckow (p. 156), if the operation is conducted at ordinary temperatures. To determine the iron in the solution from which the copper has been removed, it is evaporated to dryness with the addition of sufficient sulphuric acid to convert the iron into sulphate, and the double oxalate is prepared by the method given on page 138.

EXPERIMENT.

Used about 1 g each of copper sulphate and ferrous ammonium sulphate and 5 cc nitric acid (sp. g. 1.35). Volume of liquid, 120 cc.

Current Dens., Amperes.	Electrode Tens., Volts.	Temp.	Time, hr. m.	Found Cu.	Taken Cu.
1.0–0.9	3.0–3.3	19–32°	4 —	0.2518 g	0.2528 g
1.1–1.0	2.6–3.2	18–32°	3 30	0.2430 "	0.2450 "

The free sulphuric acid in the decanted liquid was neutralized with ammonium hydroxide, and 8 g ammonium oxalate were added.

Current Dens., Amperes.	Electrode Tens., Volts.	Temp.	Time, hr. m.	Found Fe.	Taken Fe.
1.30–0.8	2.7–4.5	31–42°	3 —	0.1416 g	0.1406 g
1.45–1.1	3.0–3.5	60°	3 30	0.1438 "	0.1435 "

A similar separation may also be carried out in the presence of sulphuric acid instead of nitric acid. Three cubic centimeters of the concentrated acid are used, the other conditions being the same.

Current Dens., Amperes.	Electrode Tens., Volts.	Temp.	Time, hr. m.	Found Cu.	Taken Cu.
1.05–1.20	3.0–2.85	22–30°	2 10	0.2534 g	0.2539 g
1.00–0.95	2.5–2.45	56–59°	2 —	0.2504 "	0.2510 "

The determination of the iron was conducted as before.

				Fe.	Fe.
1.55–1.32	3.4–3.8	33–40°	4 —	0.1419 g	0.1421 g
1.60–1.40	3.0–3.5	61–64°	3 —	0.1625 "	0.1675 "

The separation of iron and copper may be performed if the copper is precipitated from a hot solution of the double oxalate containing free oxalic, tartaric, or acetic acid. A saturated solution of oxalic acid is used, and one of tartaric acid which contains 6 g acid in every 100 cc.

EXPERIMENT.

Used about 1 g each of copper sulphate and ferric salt, 6 g ammonium oxalate. The copper must be washed without interrupting the current.

Amperes.	Volts.	Temp.	Time.	Found Cu.	Taken Cu.
1.1–1.0	2.95–3.5	51–62°	3 hr.	0.2525 g	0.2528 g
0.7–0.7	3.20–2.85	62°	3 "	0.2532 "	0.2530 "

The iron was determined in the solution which was poured off from the copper, the free acid being first neutralized with ammonium hydroxide.

				Fe.	Fe.
1.4–1.3	3.0–3.2	68–70°	2½ hr.	0.1431 g	0.1435 g
1.0–0.9	3.1–3.3	30–40°	3 "	0.1425 "	0.1429 "

Vortmann dissolves the oxides of both metals in an ammoniacal solution, to which are added several grams of ammonium sulphate, and electrolyzes with a current of $ND_{100} = 0.1–0.6$ ampere. Only copper is precipitated, the ferric hydroxide remaining unaltered in solution.

Iron—Lead.

The separation is based on the separation of lead as peroxide in the presence of nitric acid (p. 168). The iron is determined as above.

COBALT.

Cobalt—Zinc.

LITERATURE:

Vortmann, Elektrochem. Zeit., **1**, 6.
Smith and Wallace, Journ. of anal. Chem., 1893, p. 183.

According to Vortmann, an excess of a 10–20% solution of sodium hydroxide is added to the solution containing the metals. Several grams of sodium potassium tartrate are then added and the electrolysis is conducted with a current of $ND_{100} = 0.07–0.1$ ampere and an electrode tension of 2 volts. The cobalt is precipitated, but the addition of potassium iodide is necessary in order to prevent the separation of cobaltic oxide at the anode.

Cobalt—Aluminium.

The method is carried out similarly to that of iron from aluminium.

Cobalt—Uranium; Cobalt—Chromium; Cobalt—Uranium—Chromium.

The methods employed are similar to those of the corresponding separations from iron (p. 200).

Cobalt—Copper.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **27**. 2060.
Rüdorff, Zeit. f. angew. Chem., 1894, p. 388.
Warwick, Zeit. f. anorg. Chem., **1**, 299.

The separation of these two metals can only be satisfactorily carried out by the electrolysis of solutions containing oxalic, tartaric, or dilute acetic acid, at a temperature of 50–60°, and at an electrode tension of not less than 1.1 or more than 1.3 volts. In order to have the tension constant and to be able to regulate it conveniently, it is best to insert the wire-gauze resistance described on page 113 in the main circuit.

EXPERIMENT.

Used 1 g copper sulphate, 1 g cobalt ammonium sulphate, and 6 g ammonium oxalate.

Electrode Tension, Volts.	Temp.	Time, hr.	Time, m.	Found* g Cu.	Found* % Cu.
1.24–1.30	50–60°	3	50	0.2602	25.36
1.20–1.35	50–60°	3	30	0.2531	25.29
1.20–1.29	50–60°	4	—	0.2522	25.28

Cobalt—Bismuth.

LITERATURE:

Smith and Wallace, Journ. of Anal. Chem., 1893, p. 183.
Smith and Moyer, Zeit. f. anorg. Chem., **4**, 268.

According to Smith and Wallace, and also Smith and Moyer, a separation of these metals may be satisfactorily conducted in a solution containing nitric acid. Since, however, the required conditions of experiment are not given in the respective publications, the methods will be here omitted.

* [Theory 25.33% Cu.]

Cobalt—Lead.

The solution, to which nitric acid has been added, is electrolyzed (see Lead).

Cobalt—Mercury.

Similar to the above.

NICKEL.

Nickel—Manganese.

What has been said with reference to the separation of iron from manganese applies also to the separation of nickel from manganese.

Nickel—Aluminium.

Similar to the separation of iron from aluminium.

Nickel—Uranium ; Nickel—Chromium.

See Iron (pp. 198–199).

Nickel—Copper.

LITERATURE :

Classen, Ber. deutsch. chem. Ges., 27, 2060.

The separation takes place under the same conditions as the separation of cobalt from copper.

If 1 g each of copper sulphate and nickel sulphate are taken, 6 g ammonium oxalate are required. Larger quantities of metal require correspondingly greater quantities of the ammonium oxalate.

EXPERIMENT.

Elec. Tens., Volts.	Time, hr. m.	Found* g Cu.	Found* % Cu.	Remark.
1.11–1.3	3 50	0.2552	25.40	
1.20–1.3	3 —	0.2559	25.37	Acidified with oxalic acid.
1.20–1.3	3 30	0.2591	25.38	Acidified with tartaric acid.
1.34–1.45	3 50	0.2579	25.45	Acidified with acetic acid. The copper contained nickel.
1.20–1.6	3 50	0.2595	25.33	The copper contained nickel.

Nickel—Lead.

The separation corresponds to the method given under Cobalt.

Nickel—Mercury.

LITERATURE:

Rudörff, Zeit. f. angew. Chem., 1894, p. 388.
Smith, Am. Chem. Journ., **12**, 104.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1585.

The method for the separation of these two metals is similar to that of cobalt from mercury. According to the statements of Smith, the separation may be carried out from a solution of the double cyanides. Heidenreich, who determined in the Aachen laboratory the proper conditions of experiment, found that only the mercury is precipitated when the tension at the electrodes is 1.2–1.6 volts.

EXPERIMENT.

Used about 1 g nickel ammonium sulphate and 3 g potassium cyanide.

Taken g $HgCl_2$.	Current Density, Amperes.	El. Tension, Volts.	Time.	Found† per cent Hg.
0.3687	0.08–0.03	1.2–1.6	5½ hr.	73.65
0.3702	0.05–0.93	1.4–1.5	overnight	73.62
0.3000	0.05–0.03	1.4–1.5	"	73.66

*[Theory 25.33% Cu.] †[Theory 73.80% Hg.]

ZINC.

Zinc—Manganese.

This separation, similar to that of copper from cobalt, takes place from hot solutions containing free oxalic acid, which prevents the separation of manganese peroxide.

Zinc—Aluminium.

Conditions similar to the above.

Zinc—Copper.

LITERATURE:

Rüdorff, Zeit. f. angew. Chem., 1893, p. 452.
Smith and Wallace, Journ. of Anal. Chem., 1893, p. 183.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1585.

For this separation, Smith and Wallace recommend the precipitation of the copper from a solution to which nitric acid has been added. Heidenreich, who determined in the Aachen laboratory the proper conditions of experiment, found that if the solution contains about 4 cc nitric acid (sp. g. = 1.3) to 120 cc of liquid, and the tension of 1.4 volts is not exceeded, the copper only is precipitated. The greater part of the copper separates in a short time, but the precipitation of the last trace proceeds very slowly. The analysis therefore requires from 18 to 20 hours.

EXPERIMENT.

Used copper sulphate (containing 25.29% Cu) to which was added 0.8 g zinc ammonium sulphate.

Taken $CuSO_4.5H_2O$, g.	Current Density, Amperes.	Electrode Tension, Volts.	Time, hr.	m.	Found Cu, %	
0.4476	0.2	1.00–1.10	6	30	24.31	
0.3857	0.2–0.3	1.00–1.20	8	—	25.00	
0.4244	0.2	1.00–1.15	15	30	25.19	
0.4689	0.2	1.00–1.15	15	30	25.25	
0.4728	0.2–0.15	1.00–1.20	18	—	25.25	
0.5049	0.20–0.15	1.13	18	—	25.31	
0.4660	0.5	1.20	2	—	25.22	
0.4775	1.05–0.9	1.50	2	—	25.84	contained
0.4826	1.00–0.8	1.35–1.98	18	—	25.80	zinc
0.4576	0.50–0.4	1.15–1.23	6	30	25.19	

Zinc—Cadmium.

LITERATURE.

Smith, Am. Chem. Journ., **11**, 352.
Yver, Bull. Soc. Chem., **34**, 18.
Eliasberg, Zeit. f. anal. Chem., **24**, 550.
Smith and Knerr, Am. Chem. Journ., **8**, 210.

A. Yver recommends the use of a solution of the acetates or sulphates treated with an excess of sodium acetate and a few drops of acetic acid; the electrolysis to be conducted hot, using two Daniell cells.

In the laboratory of the Technical High School in Munich the following directions are given for Yver's method: To the sulphuric acid solution of the two metals add sodium hydroxide solution until a permanent precipitate is obtained, dissolve the precipitate in the smallest possible quantity of dilute sulphuric acid, dilute the solution to about 70 cc, and reduce the cadmium with a current of $ND_{100} = 0.07$ ampere. When the greater part of the metal is precipitated, neutralize the free sulphuric acid with sodium hydroxide, add 3 g sodium acetate, heat to about 45°, and subject to the action of a current of $ND_{100} = 0.3$ ampere. The latter direction assumes that the electromotive force is not over 3.6 volts; if more, it is to be reduced to about 2.4 volts.

Zinc—Lead.

The separation is conducted from a nitric acid solution, the lead being precipitated as peroxide (see Lead, p. 168). To determine the zinc, it is converted into the sulphate in the manner described under the separation of iron from copper on page 202, and is precipitated by the method given on page 146.

Zinc—Silver.

LITERATURE:

Smith and Wallace, Zeit. f. Elektrochemie, **2**, 312;
Journ. of Anal. Chem., 1892, p. 87.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1585.

The separation, according to Smith and Wallace, is conducted from a solution of the double cyanide. The proper experimental conditions were acertained by Heidenreich in the Aachen laboratory, with the result that the separation was best carried out at a temperature of 60–70°, and with a tension at the electrodes of 1.9–2 volts.

EXPERIMENT.

Taken g $AgNO_3$.	Current Density, Amperes.	Electrode Tens., Volts.	Temp.	Time.	Found* % Ag.
0.4046	0.05	1.9–2.03	60°	28 hr.	63.34
0.4149	0.03	2.1–2.05	"	22 "	63.31
0.3260	0.08	1.9	"	16 "	63.23
0.3739	0.08–0.05	2.0–2.15	"	15 "	63.31
0.2949	0.05–0.02	1.8–2.05	"	$6\frac{1}{2}$ "	63.36

Zinc—Mercury.

LITERATURE:

Smith and Wallace, Zeit. f. Elektrochemie, **2**, 312.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1585.

Smith and Wallace conduct the separation from a solution of the double cyanide. According to the experiments carried

*[Theory 63.52% Ag.]

out in the Aachen laboratory by Heidenreich, the mercury is precipitated free from zinc.

In performing the experiments, Heidenreich observed also that the dishes used suffer severely from the combined action of the mercury and potassium cyanide on the platinum.

EXPERIMENT.

Taken g $HgCl_2$.	g KCN.	Current Density, Ampere.	Elec. Tension, Volts.	Time.	Found* %Hg.
0.2501	2–3	0.08–0.04	1.65–1.69	5 hr.	73.61
0.2655	2–3	0.03	1.75	14 "	73.51

MANGANESE.

Manganese—Copper.

The separation is conducted similarly to that of copper from cobalt. The copper is precipitated from a hot solution containing free oxalic acid which prevents the separation of manganese peroxide. The liquid containing the manganese is poured off from the copper. Generally this is not suited for direct electrolytic determination, since the substances previously added interfere with the precipitation of the manganese, and the volume of the liquid has become too great as a result of washing the copper without interrupting the current. According to the directions of Jannasch the manganese is then precipitated with ammonia and hydrogen peroxide. The precipitate is allowed to settle and the solution is filtered. The precipitate is dissolved in a mixture of 5 cc of acetic acid, 5 cc hydrogen peroxide, and 25 cc water, and this solution is submitted to electrolysis after the excess of hydrogen peroxide has been removed with chromic oxide. The same method is employed when the solution contains manganese chloride, since the presence of the chlorine also interferes with the separation of the peroxide.

The following experiment was performed as above directed by Dr. Carl Engels in the Aachen laboratory.

* [Theory 73.80% Hg.]

EXPERIMENT.

The solution contained $(NH_4)_2MnCl_4.7H_2O$.

$(NH_4)_2MnCl_4.7H_2O$ taken, g.	Current Density, Amp.	Electrode Tension, Volts.	Temp.	Time, hr.	Time, m.	Found* Mn_3O_4, g.	Found* Mn_3O_4, %
0.8619	0.63	2.8	80°	1	45	0.2153	24.98
0.9550	0.62	2.8	82°	1	45	0.2385	24.98
0.9562	0.70	2.9	83°	1	45	0.2394	25.03
1.0131	0.72	3.1	80°	1	30	0.2536	25.03
0.8580	0.80	3.1	80°	1	15	0.2151	25.01
1.1383	0.78	3.1	85°	1	15	0.2848	25.02

Manganese—Cadmium.

This is conducted similarly to the separation of manganese and copper, and the manganese is determined according to the directions of Engels, which are given above.

COPPER.

Copper—Cadmium.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1585.
Smith and Wallace, Journ. of Anal. Chem., 1893, p. 183.
Smith and Moyer, Zeit. f. anorg. Chem., **1**, 299.

According to the statements of Freudenberg, the two metals may be separately precipitated from a sulphuric acid solution (10–20 cc. of dilute sulphuric acid) by a variation of the tension. With a tension of 2 volts the copper is precipitated, all the cadmium remaining in solution.

Heidenreich tested this method in the Aachen laboratory, and found that the separation is best conducted with a tension not exceeding 1.85 volts.

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* [It seems probable that the salt taken was not pure. $MnCl_2.2NH_4Cl.7H_2O$ contains 21.27% of Mn_3O_4.—*Trans.*]

EXPERIMENT.

The volume of the liquid was 120 cc, containing 15 cc dilute sulphuric acid (sp. gr. = 1.09).

Taken $CuSO_4.5H_2O$, g.	Taken $CdSO_4.8H_2O$, g.	Current Density ND_{100}, Amperes.	Electrode Tension, Volts.	Time, hrs.	Found* Cu, %
0.7078	0.4	0.07–0.05	1.7–1.76	24	25.27

Experiments in which it was attempted to replace the sulphuric acid by nitric acid yielded no satisfactory results.

Copper—Lead.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **27**, 2060.
Nissenson, Zeit. f. angew. Chem., 1893, p. 452.

To separate copper from lead, 20 cc of nitric acid (sp. g. 1.35) are added to the solution, which is then diluted to 75 cc, warmed and electrolyzed with a current of 1.1–1.2 amperes (corresponding to $ND_{100} = 1.5$–1.7 amperes). At the end of one hour the greater part of the lead has separated as peroxide (98–99% when not more than 0.5 g is present in the solution), and the current is then interrupted, no trace of copper as yet appearing at the cathode. The liquid is then transferred to a second tared dish, the lead peroxide is washed with water, and after drying is weighed. The washings from the lead peroxide are added to the copper solution, which is then treated with ammonium hydroxide until the well-known deep blue color appears, and about 5 cc nitric acid are added. The platinum dish is connected with the negative pole of the source of current, and one of the perforated platinum bucket electrodes, described by the author, is employed as anode to

* [Theory 25.33% Cu.]

take up the remainder of the lead peroxide. This electrode should have a roughened surface. It is weighed before the experiment. After the solution has cooled, it is diluted to 120–150 cc, and electrolyzed with a current of $ND_{100} = 1.0$–1.2 amp. At the end of 3 to 4 hours the copper (if about 0.25 g is present), together with the rest of the lead, is precipitated.

This method, which is of great value in technical work, is not only rapid (4–5 hours as compared to 14 hours or more), but allows of the complete precipitation of both metals, irrespective of the relative quantities present.

When this method is employed for the analysis of substances containing sulphur, the lead sulphate resulting from the oxidation is troublesome. The operation of dissolving this may often require more time than the analysis itself.

Accordingly, if lead sulphate is formed, either as a result of the oxidation of sulphur or of double decomposition between lead nitrate and copper sulphate, a slight excess of ammonia is added and the solution is warmed for several minutes. The dense lead sulphate is hereby converted into porous lead hydroxide. The liquid is poured little by little into the platinum dish, which contains about 20 cc of warm nitric acid, and constantly stirred with the electrode. The lead sulphate which reappears either dissolves immediately, or if the quantity is large the greater part of it goes immediately into solution, and the remainder disappears on warming for a short time. The vessel in which the decomposition of the lead sulphate is conducted is first washed with a little nitric acid and then with water.

EXPERIMENT.

Used about 1 g each of lead nitrate and copper sulphate, and 20 cc nitric acid.

Current Density, Amperes.	Electrode Tension, Volts. Beginning.	End.	Temp.	Time, hr.	Found PbO_2, g.	Taken PbO_2, g.
1.1 –1.1	1.4	1.4	60–63°	1	0.7266	0.7260
1.55–1.45	1.4	1.4	66–72°	1	0.7310	0.7303

The liquid was poured off from the lead peroxide, made alkaline with ammonia, and 5 cc. nitric acid were added. The copper was then separated by electrolysis.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time, hr.	Found Cu, g.	Taken Cu, g.
1.1–1.0	2.2 –2.5	25–30°	5	0.2490	0.2495
1.0–0.95	2.25–2.3	30–32°	5	0.2505	0.2510

H. Nissenson, who employed the preceding method for determining the copper and lead in copper matte, gives the following directions for carrying out the analysis:

1 g copper matte is dissolved in 30 cc nitric acid (sp. g. 1.4) and the solution is diluted to 180 cc. The electrolysis is so conducted that the lead is precipitated on the dish, a perforated platinum plate which serves as cathode receiving the copper. The electrolysis is started at ordinary temperatures with a current density of 0.5 ampere, which at the end of an hour is increased to 1.5–2 amperes. Both metals are completely precipitated in 6–7 hours.

For technical analyses, where the determination is conducted from nitric acid solutions, the presence of small quantities of silver and bismuth may be neglected. Where lead is precipitated from nitric acid solutions containing arsenic, selenium, or manganese, even in very small quantities, the results are not accurate.

Copper—Silver.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.
Smith and Wallace, Zeit. f. Elektrochemie, **5**, 312.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1585.

Freudenberg employs a solution containing a few cubic centimeters of nitric acid (sp. g. 1.2) for the separation of the silver, which is quantitatively precipitated at a tension of 1.3–1.4 volts. The copper remains in solution and is first decomposed at a higher tension (2–3 volts).

According to E. Smith, these two metals may be separated from a solution of the double cyanides. 4.5 g of potassium cyanide are added to a solution of about 0.4 g of the mixed metals. The solution is diluted to about 120 cc and electrolyzed. If the solution be warmed to 65–75°, the precipitation of the silver is greatly hastened. M. Heidenreich tested this method in the Aachen laboratory and determined the following conditions of experiment.

EXPERIMENT.

Used silver nitrate containing 63.42% silver, and copper sulphate. About 0.7 g of copper sulphate was added.

Taken g $AgNO_3$.	g KCN.	Current Density, Amperes.	Electrode Tension, Volts.	Time, hr.	m.		Found % Ag.
0.2379	2	0.07–0.03	1.0–1.2	8	—		63.34
0.2303	2	0.04	1.0–1.28	8	—		63.43
0 3099	2	0.03	1.0–1.39	6	30		63.40
0.3327	2	0.09	1.2–1.3	4	—	warmed	63.27
0.6037	6	0.19–0.08	1.2–1.3	6	—		63.33

Copper—Mercury.

LITERATURE:

Smith, Journ. of Anal. Chem., **3**, 254; **5**, 489.
Am. Chem. Journ., **11**, 104, 264.
Freudenberg, Zeit. f. phys. Chem., **12**, 113.

According to E. Smith, the separation may be conducted from a solution of the double cyanides. The temperature

should be about 65°. With the ordinary conditions of concentration, about 2 g potassium cyanide are added, and the solution is electrolyzed with a current of $ND_{100} = 0.06–0.08$ ampere. The decomposition requires about 4 hours for every 0.2 g of the combined metals. The copper remains in solution, the mercury being deposited.

Freudenberg found that at a tension of 2.5 volts the mercury, in the presence of 2–4 g potassium cyanide, separates brilliantly white and completely free from copper.

Copper—Arsenic.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.
Schmucker, Zeit. f. anorg. Chem., **5**, 199.

Although formerly it was necessary to remove the arsenic before precipitating the copper, Freudenberg has shown that a separation may be satisfactorily conducted from a sulphuric acid solution (10–20 cc dilute sulphuric acid) if the tension is not allowed to exceed 1.9 volts. It is immaterial whether the arsenic is added in the form of trioxide or pentoxide. A second method of the same author is the following: Ammonia is added to the solution containing the metals in the form of higher oxides, until there is an excess of about 30 cc of a 10% ammonia solution. The electrolysis is conducted with a current tension of 1.9 volts, and is continued until the solution is completely decolorized, requiring generally 6–8 hours.

This method is not suitable for the separation of copper and antimony.

CADMIUM.

Cadmium—Lead.

This process is the same as the separation of lead from copper. The lead is separated as peroxide from a nitric acid

solution. To determine the cadmium in the solution from which the lead has been removed, the nitric acid is evaporated off on the water-bath, the cadmium converted into sulphate, and treated according to the directions on page 164.

Cadmium—Mercury.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.

According to Freudenberg, the separation proceeds best from a solution of the salts of both metals, containing 0.5–1 g potassium cyanide. With a tension of 1.8–1.9 volts mercury only is precipitated. After the separation of the mercury, the cadmium is precipitated from the solution by a current of higher tension.

LEAD.

Lead—Silver.

This separation is conducted like that of lead from copper (see page 213). To determine the silver, the solution is evaporated down on the water-bath, and the silver is precipitated according to the directions given on page 173.

Lead—Mercury.

LITERATURE:

Smith and Moyer, Zeit. f. anorg. Chem., **4**, 267.
Heidenreich, Ber. deutsch. chem. Ges., **28**, 1585.

The method corresponds to that used for the separation of copper from lead. Smith and Moyer attempt to determine the lead and mercury at the same time. They add 5 cc nitric acid (sp. g. 1.3) to the solution of the two metals, and dilute the liquid to 180 cc. The electrolysis is con-

ducted with a current of 1.7 cc of oxyhydrogen gas per minute.

Heidenreich determined the conditions of experiment for the preceding method, and found that 20–30 cc nitric acid (sp. g. 1.3–1.4) must be present for every 120 cc of the solution to be electrolyzed, since otherwise the lead peroxide scales off and cannot be accurately determined. A current of $ND_{100} = 0.2–0.5$ ampere may be used. The fact that greater quantities of lead could not be precipitated in an adherent form was due to the condition of the surface of the platinum disk which was used as anode.

Lead—Antimony.

LITERATURE:

Neumann and Nissenson, Chemiker Zeitung, 1895, No. 49.

For the electrolytic determination of both metals in alloys (stereotype-metal, type-metal), Neumann and Nissenson recommend that 2.5 g of the alloy be dissolved by warming with a mixture of 10 g tartaric acid, 4 cc nitric acid (sp.g. 1.4), and 15 cc water. 4 cc conc. sulphuric acid are then added, the solution is diluted with water, allowed to cool, and filled up to exactly one quarter liter. If the liquid is now filtered off from the separated lead sulphate, it will contain all of the antimony. 50 cc of this filtrate are made strongly alkaline with sodium hydroxide, 50 cc of a saturated solution of sodium monosulphide are added, the solution is filtered immediately, washed from the precipitate, and electrolyzed according to the method given on page 180.

For the determination of the lead, the lead sulphate is treated as in the separation of lead from copper (page 213).

SILVER.

Silver—Antimony.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.

If the antimony is present as pentoxide, the separation may be carried out from an ammoniacal solution to which several grams of ammonium sulphate have been added.

The silver is precipitated at a tension of 1.7–1.8 volts.

Silver—Arsenic.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.

According to Freudenberg, this separation is conducted in the same manner as the separation of silver from antimony.

MERCURY.

Mercury—Antimony.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.

The antimony must be added in the form of a pentavalent salt, since a reduction of the mercuric salt present would otherwise occur. A mixture of the chlorides of the two metals is brought into solution by the use of 0.5–1 g tartaric acid. The solution is diluted with water, made neutral with ammonia, and then about 20 cc of a 10% solution of ammonia are added until the solution is perfectly clear. The electrolysis is conducted at a tension of 1.6–1.7 volts. After the mercury

is deposited, the solution is made acid and hydrogen sulphide is passed in. The antimony sulphide may be either directly determined, i.e., weighed, or determined by electrolysis (see page 179).

Mercury—Arsenic.

LITERATURE:

Freudenberg, Zeit. f. phys. Chem., **12**, 97.

According to Freudenberg, the separation is conducted from a nitric acid solution (see page 175) from which the mercury is precipitated at a tension of 1.7–1.8 volts.

ANTIMONY.

Antimony—Tin.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **17**, 2245; **18**, 1110; **28**, 2060.

The separation of antimony from tin by the ordinary gravimetric methods, which, as is well known, is difficult, and gives uncertain results, may be accomplished by electrolysis with ease and accuracy. Antimony may be completely precipitated, in the presence of tin, from a *concentrated* solution of sodium sulphide, to which is added a certain amount of sodium hydroxide.

The crystallized sodium monosulphide of commerce, aside from the fact that its purity is otherwise uncertain, is not pure monosulphide, but is a mixture of several sulphides with varying amounts of sodium hydroxide. This explains the large amount of alumina which it always contains. If, therefore, commercial sodium sulphide is to be used, it must first be dissolved, and the solution, with exclusion of air, completely saturated with pure hydrogen sulphide gas. It is then filtered from the precipitated impurities, and evaporated in a

large platinum or porcelain dish. The further treatment is given in full in the chapter on reagents. As the condition of the sodium sulphide solution is of great importance to the success of the process, it is preferable to prepare the solution as directed in the chapter referred to.

The process of separation is as follows: A mixture of the pure sulphides,* or the residue obtained by evaporating a solution of the two metals, is treated in a platinum dish with about 80 cc of a sodium sulphide solution saturated at ordinary temperatures, and enough *concentrated* solution of pure sodium hydroxide† to furnish 1–2 g NaOH. If solution does not take place at once, it is hastened by heating over a low flame, the watch-glass covering the dish is rinsed with 10–15 cc water, and the solution is allowed to *cool thoroughly*. It is then submitted to electrolysis.

When weak currents ($ND_{100} = 0.2$ amp.) are employed, the separation of the antimony requires about 14 hours, so that the electrolysis must be continued through the night. Experiments recently undertaken by the author have shown that, for the precipitation of antimony in the presence of tin, the solution may be warmed to 50–60° and a current density of $ND_{100} = 0.5$ ampere employed. It is thus possible to complete the precipitation within 2 hours.

When the action begins, the whole surface of the dish, which is in contact with the solution, becomes quickly covered with a dark coating of antimony, which soon takes on a brilliant metallic appearance.

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* The solution of a mixture of the metallic sulphides and sulphur in sodium sulphide is to be treated like a solution of polysulphides (see further on).

† The sodium hydroxide used must be absolutely pure, and must show no cloudiness when warmed with sodium sulphide. Otherwise the results obtained for the antimony will be too high, owing to the inclusion of the precipitate.

In the earlier part of the process, the entire solution appears to be filled with small gas-bubbles which rise slowly, break at the surface, and cover the watch-glass with minute portions of the solution. In the course of two hours the disengagement of gas is ended, and the solution is completely clear. To avoid loss, it is best, at this time, to wash repeatedly the under surface of the watch-glass with a drop of water which is finally allowed to run down the positive electrode. When the reduction is completed, the antimony is washed without interrupting the current, and is treated according to the directions already given (p. 180).

As tin cannot be reduced from a sodium sulphide solution (as stated on p. 184), but can be completely precipitated from solution in ammonium sulphide, the sodium sulphide, after the separation of antimony, must be converted into ammonium sulphide according to the directions given on p. 187.

If the two metals are to be determined in the yellow solution of polysulphides of the alkalies, the solution is decolorized with ammoniacal hydrogen peroxide (see Antimony, p. 181), and evaporated nearly to dryness; about 80 cc sodium sulphide solution and the necessary amount of sodium hydroxide are then added, and the process carried on as above directed.

In the following experiment, antimony was precipitated from both warm and cold solutions containing tin.

EXPERIMENT.

Used about 1 g antimony potassium tartrate, an equal quantity of $NH_4Cl.SnCl_4$, 80 cc sodium sulphide solution, and about 2 g sodium hydroxide.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time, hrs.	Found Sb, g.	Taken Sb, g.
1.5–1.45	0.9–0.8	57–67°	2	0.3790	0.3780
1.5–1.6	0.8–0.9	58–60	2	0.3787	0.3780
0.4–0.2	0.7–0.55	30–24	15	0.3775	0.3780

The antimony precipitate appeared gray and shiny, and contained no tin.

Antimony—Arsenic.

LITERATURE:

Classen and Ludwig, Ber. deutsch. chem. Ges., **19**, 323.

In an *alkaline* solution, arsenions acid is oxidized to arsenic acid by the galvanic current. If, however, a solution containing antimony and arsenious acid is electrolyzed, a mixture of antimony with arsenic is deposited. The action is different if the arsenic is present in the solution as *arsenic* acid; in the presence of a free alkali, the antimony alone is deposited from a concentrated sodium sulphide solution. The arsenic, therefore, if present as arsenious acid, must be oxidized to arsenic acid before the metals can be separated. It is heated with concentrated nitric acid or aqua regia, the acid completely removed by evaporation on the water-bath, the residue treated with 80 cc of a cold saturated sodium sulphide solution, a concentrated solution of sodium hydroxide (containing about 1—2 g NaOH) added, and the solution electrolyzed. The separation is conducted precisely like that of antimony from tin.

The electrolysis may be conducted either warm or at ordinary temperatures. If antimony and arsenic are to be determined in a solution of polysulphides of the alkalies, the solution is treated as described on p. 181. To determine arsenic, the antimony-free solution is acidified with dilute sulphuric acid, heated in the water-bath to remove hydrogen sulphide,

filtered, and the precipitate dissolved in hydrochloric acid with the addition of potassium chlorate. This solution is treated with ammonia in excess, and the arsenic acid precipitated as magnesium ammonium arsenate with magnesium mixture.

The precipitate may be dried, at 110°, on a weighed filter, and weighed, or converted into magnesium pyro-arsenate by careful ignition in a porcelain crucible.

EXPERIMENT.

Used about 1 g of antimony potassium tartrate, 1 g sodium arsenate, 80 cc sodium sulphide solution, and 2.5 g sodium hydroxide.

Current Density, Amperes.	Electrode Tension, Volts.	Temp.	Time, hr. m.	Found Sb, g.	Taken Sb, g.
1.55–1.5	1.75–1.1	54–57°	3 30	0.3778	0.3773
1.60–1.5	2.10–1.45	25–38	6 —	0.3770	0.3773
0.5 –0.4	1.75–0.8	21–24	overnight	0.3770	0.3770

Antimony—Tin—Arsenic.

LITERATURE:

Classen, Ber. deutsch. chem. Ges., **17**, 2245; **18**, 1110; **28**, 2060.
Classen and Ludwig, *ibid.*, **19**, 323.

If arsenic is present as arsenic acid, antimony alone is precipitated from a concentrated alkaline solution of the three metals in sodium sulphide; tin and arsenic remain in solution. The arsenic is converted into arsenic acid, and the antimony precipitated, exactly as heretofore described.

For the separation of tin from arsenic, the solution poured off from the antimony is treated with dilute sulphuric or hydrochloric acid to decompose the sulpho-salts, the mixture of arsenic and tin sulphides and sulphur is filtered off and oxidized with hydrochloric acid and potassium chlorate, and

the arsenic separated as described below. To determine the tin, the solution freed from arsenic is saturated with hydrogen sulphide, filtered, and the tin sulphide dissolved in ammonium sulphide. The tin is determined electrolytically as directed p. 186.

In the analysis of a substance which contains arsenic, antimony, and tin, the arsenic may also be first eliminated according to the method of E. Fischer-Hufschmidt simplified by R. Ludwig and the author,* and antimony and tin separated in the arsenic-free solution.

If the sulphides of the metals are to be separated, they are oxidized with concentrated hydrochloric acid and potassium chlorate, and the acid evaporated on the water-bath. The residue is washed with fuming hydrochloric acid into a flask of 500–600 cc capacity,† treated with 20–25 cc of a saturated solution of ferrous chloride, or, better with about 25 g of ammonium ferrous sulphate [$FeSO_4.(NH_4)_2SO_4.6H_2O$], and fuming hydrochloric acid added till the volume is 150 to 200 cc. A strong current of hydrochloric acid gas is now passed into the solution, and kept up for at least half an hour after the solution seems fully saturated. Then the solution is reduced to about 50 cc by distilling off the liquid, without a condenser, in a stream of hydrogen chloride gas. A flask of about 1 liter capacity, containing 400–500 cc water, is used as a receiver. If the flask is well cooled during the distillation, not a trace of arsenic passes over into a second receiver, even when as much as 0.5 g, reckoned as As_2O_3, is present.

The arsenic in the distillate may either be saturated with sodium carbonate and titrated with iodine solution, or pre-

* Ber. d. ch. Ges., 18, 1110.

† A convenient apparatus is illustrated in the author's "Handbuch der Quantitative Analyse," 4th edition, p. 78.

cipitated as As_2S_3 with hydrogen sulphide, and determined as such on a weighed filter, or the arsenic calculated from the amount of sulphur in the precipitate. The process, in the latter case, is as follows: The distillate is mixed with twice its volume of water, air expelled by a strong current of carbon dioxide, and the arsenic precipitated by passing in pure hydrogen sulphide gas. The excess of hydrogen sulphide is removed by passing a strong current of carbon dioxide till lead acetate paper is not colored by the escaping gases. The arsenic sulphide is allowed to subside, and the clear solution siphoned off. The remaining strongly acid solution is saturated with ammonia, which dissolves the arsenic sulphide; the solution is then boiled with an excess of hydrogen peroxide free from sulphuric acid. The solution is acidified with hydrochloric acid, and the sulphuric acid produced by the action of the hydrogen peroxide determined as barium sulphate in the usual way (Classen).

To determine the antimony and tin, the strong acid solution in the flask, which contains the iron, is diluted with three times its volume of water. Antimony and tin are precipitated with hydrogen sulphide. After the precipitate has subsided, the clear solution is poured on a filter, the precipitate washed several times by decantation, and afterwards, on the filter, with hot water, till free from hydrochloric acid. Portions of the sulphides often adhere to the walls of the flask in which the precipitation took place. These are washed out with concentrated sodium sulphide solution, and the solution is poured on the filter containing the sulphides. The filtrate is collected in a weighed platinum dish. The filter, on which some iron sulphide always remains after the solution of the antimony and tin sulphides, is washed with sodium sulphide solution, the necessary amount of sodium hydroxide is added

to the filtrate, and the antimony and tin are separated electrolytically as already directed.

TIN—PHOSPHORIC ACID.

In the determination of metals, in the presence of phosphoric acid, the latter is often removed as tin phosphate. The phosphoric acid is then usually determined in a separate portion, as its determination in the tin precipitate is too difficult and slow a process. The precipitate of tin oxide and tin phosphate may, however, be dissolved by digesting with ammonium sulphide, the solution diluted, the tin precipitated by electrolysis, and the phosphoric acid determined as usual.

PLATINUM—IRIDIUM.

As stated on page 182, platinum can be separated from a hydrochloric acid solution by a current of $ND_{100} = 0.05$ ampere and 1.2 volts.

This property of platinum may be used for separating it from iridium, which under similar conditions remains in solution.

The platinum is deposited free from iridium. (Classen.)

SEPARATION OF GOLD FROM OTHER METALS.

LITERATURE:

Smith and Muhr, Ber. deutsch. chem. Ges., **23**, 2175.
Smith and Wallace, *ibid.*, **25**, 779;
Journ. of Anal. Chem., 1892, p. 87.

As has already been frequently stated, Edgar F. Smith has made an exhaustive study of the action of the galvanic current on the cyanides of the metals, and has applied this

method to the separation of gold from palladium, copper, nickel, zinc, and platinum.

The same conditions may also be employed for the separation of silver from platinum and mercury from platinum.

Smith gives but incompletely the conditions of experiment necessary for conducting these operations, and therefore a consideration of them in detail will be omitted.

POTASSIUM—SODIUM.

The ordinary method of determining potassium and sodium in the same solution is to weigh the mixed chlorides, and the potassium as platinchloride; the sodium is thus determined by difference. The errors of the work, therefore, all fall on the sodium. The potassium may be determined, as already directed (p. 188), by precipitating as potassium platinchloride, and determining the platinum in the latter by electrolysis. To determine the sodium directly, the filtrate from the potassium platinchloride is evaporated on the water-bath to remove alcohol, the residue dissolved in water with the addition of a little hydrochloric acid, and the platinum removed by electrolysis. The sodium chloride in the solution poured off from the platinum is determined by evaporating to dryness, and weighing the residue.

SODIUM—AMMONIUM.

The direct determination of both is accomplished as with potassium and sodium; the ammonium is precipitated as ammonium platinchloride, and the process conducted as described above.

APPENDIX.

SOME APPLIED EXAMPLES OF ELECTRO-CHEMICAL ANALYSIS.*

BRASS.

Alloy of Copper and Zinc (Lead, Tin, Iron).

For the separation of the copper from the other metals, it is necessary to precipitate it from an acid solution. A nitric or sulphuric acid solution may be used. The employment of a solution containing free nitric acid has the disadvantage that if the action of the current is continued for too long a period after all the copper has been precipitated, the nitric acid is reduced to ammonia, and zinc is precipitated. It has the further disadvantage that enough ammonia is often formed to prevent the complete precipitation of the zinc by sodium carbonate, a method often employed in practice. The presence of nitric acid or a nitrate also prevents the electrolytic separation of the zinc. If this acid is used, therefore, the solution, after removal of the copper, must be repeatedly

* The applied examples of electro-analysis here given appeared in the third German and second English editions of this work, but are not contained in the fourth German edition. Owing to the practical advantages of these schematic outlines, the translators have thought it best to include them in the present edition, and have, at the same time, made such alterations as the recent advances along the various lines would seem to justify.

evaporated to dryness with hydrochloric acid to convert the nitrates into chlorides.

For the analysis of the alloy, 0.1–0.2 g is dissolved in as little dilute nitric acid as possible, and evaporated to dryness on the water-bath. The residue is then treated with a few cubic centimeters of water, and 20 cc nitric acid (sp. g. = 1.27) are added. The solution is now diluted to about 100 cc, and any stannic oxide which may be present is filtered off and determined gravimetrically. From the solution, the final volume of which should be 120 cc, the copper is precipitated by electrolysis according to the directions given on page 156. The current is continued as long as a drop of the solution gives a blue color with ammonia.

If lead is present in the alloy it may be determined at the same time as the copper, since it separates on the positive electrode in the form of peroxide. A weighed positive electrode is employed, and the precipitated peroxide is washed and treated according to the directions on page 169. The separated lead peroxide and copper are washed without interrupting the current.

The zinc is best determined in the solution by adding about 5 cc dilute sulphuric acid and evaporating on the water-bath until no odor of nitric acid can be detected. The residue is dissolved in a small quantity of water, and a slight excess of ammonia added. If iron is present it will be precipitated as hydroxide, which may be filtered off from the solution and determined gravimetrically. Ammonium oxalate or lactate is now added, and the separation of the zinc conducted under the conditions * given on page 147.

When a sulphuric acid solution is employed for the sepa-

* The same electrode upon which the copper has been precipitated may be used for receiving the zinc. By this the necessity of especially preparing a copper-plated electrode is avoided.

ration of the copper, it is best to first dissolve the alloy in dilute nitric acid and filter off any stannic oxide as before. An excess of sulphuric is then added, and the solution is evaporated until all nitric acid is driven off. The residue is now treated with water, any lead which is present being then found in the form of sulphate, which can be removed by filtering and determined gravimetrically. The solution is diluted to 115 cc, 5 cc nitric acid (sp. g. = 1.21) are added, and the precipitation of the copper conducted under the conditions given on page 156. After the copper has been separated, the solution is evaporated to drive off nitric acid, and the separation of the zinc is carried out as in the previous case.

SILVER COIN.

Alloy of Copper and Silver.

The alloy is analyzed by dissolving 0.1–0.2 g in dilute nitric acid, evaporating off the acid on the water-bath, dissolving the residue in water, and treating the solution according to the directions on page 216.

NICKEL COIN.

Alloy of Copper and Nickel.

About 0.4 g of the alloy, best in the form of small cuttings, is dissolved in dilute nitric acid, 8 cc of dilute sulphuric acid (50 per cent) is added, and the solution is evaporated on the water-bath until all nitric acid is removed. The residue is then taken up in 150 cc of water, and electrolyzed with a current of $ND_{100} = 1$ ampere, and an electrode tension of 2.75–3 volts.

After the removal of the copper the solution is neutralized with ammonia, an excess of 40 cc ammonia (sp. g. 0.96) is

added, and the nickel is precipitated by a current of $ND_{100} =$ 0.5–1.5 amperes, and a tension at the electrodes of 2.8–3.3 volts.

GERMAN SILVER.

Alloy of Copper, Zinc, Nickel (Tin, Lead).

For the analysis of this alloy about 0.3 g of the metal is dissolved in nitric acid, 10 cc concentrated nitric acid added, the solution diluted to 150 cc, and electrolyzed at ordinary temperatures with a current of $ND_{100} = 0.5$–1 ampere, and an electrode tension of 2.5–2.8 volts. The solution from which the copper has been removed is evaporated to dryness with sufficient sulphuric acid to convert the nitrates present into sulphates, and the residue is dissolved in water.

To the solution containing the zinc and nickel 5 g potassium sodium tartrate is added, and the solution is made alkaline with sodium hydroxide. The zinc is now precipitated with a current of $ND_{100} = 0.3$–0.6 ampere, and an electrode tension of 2 volts.* The zinc may be precipitated on the electrode bearing the copper precipitate. In this operation oxide of nickel may separate on the positive electrode, or may form in the solution in sufficient quantities to slightly discolor the precipitated zinc. This may be avoided by adding to the solution a small quantity of potassium iodide.

The solution, containing now only nickel, is acidified with sulphuric acid, an excess of ammonia added, and the nickel separated according to the directions for cobalt given on page 142. Another method is to add 25 cc ammonia and 15–20 g ammonium carbonate directly to the nickel solution, and electrolyze with a current of $ND_{100} = 0.8$–1 ampere, at a temperature of 50–60°.†

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* Vortmann, Monatsh. f. Chem., **14**, 536.

† Neumann, Analytischen Elektrolyse, Halle, 1897.

BRONZE.

Alloy of Copper and Tin.

The alloy in a finely divided form is treated with aqua regia, and the solution is evaporated to dryness. The residue is digested with a concentrated solution of sodium sulphide, the tin being dissolved. The copper sulphide which remains after filtering is washed thoroughly with sodium sulphide and then with hydrogen sulphide solution, dissolved in the proper quantity of nitric acid, and the copper precipitated under the conditions given on page 156.

The solution of tin in sodium sulphide is brought to a volume of about 150 cc, 25–30 g ammonium sulphate is added, and the solution is boiled for about one half hour to convert the sodium sulphide into ammonium sulphide (see page 187). The solution thus obtained is treated as described on page 186.

Accurate results may also be obtained* by treating 0.2–0.4 g of the alloy, best in the form of fine turnings, with 6 cc nitric acid (sp. g. = 1.5), and adding 3 cc water. When the reaction is over, the solution is heated to boiling, diluted with 15 cc boiling water, and the stannic oxide filtered off. To the solution containing the copper, 5–10 cc of nitric acid is added, and the copper is precipitated as directed on page 156. The stannic oxide is dissolved in ammonium sulphide and determined electrolytically (page 186).

PHOSPHOR-BRONZE.

Alloy of Copper, Tin, Zinc, and Phosphorus.

When the alloy is digested with concentrated nitric acid as stated under Bronze, a precipitate remains, which consists

* Neumann, l. c.

of a mixture of tin oxide and tin phosphate, with small quantities of copper oxide. It is filtered off, washed with water containing nitric acid, and heated with a concentrated solution of sodium sulphide. The residue of copper sulphide is dissolved in nitric acid, and added to the principal solution.

The tin is determined by converting the sodium sulphide into ammonium sulphide, and electrolyzing as directed p. 186. The phosphoric acid is determined in the filtrate in the usual manner.

The nitric acid solution contains the copper and zinc. They are separated according to directions for the analysis of brass (p. 231).

MANGANESE PHOSPHOR-BRONZE.

Alloy of Copper, Tin, Zinc, Manganese, and Phosphorus.

The process is similar to that given for Phosphor-Bronze; the manganese remains with the zinc, and is finally separated as directed p. 208.

SOLDER.

Alloy of Tin and Lead.

About 0.4 g of the alloy in the form of small pieces is treated with 6 cc nitric acid (sp. g. = 1.5) and 3 cc water. When the reaction is completed the solution is heated to boiling, and diluted with 15 cc hot water, the precipitate of stannic oxide allowed to settle, filtered off, and washed with water containing a little nitric acid. The stannic oxide may be determined gravimetrically, or may be dissolved in ammonium sulphide and determined by electrolysis according to the directions given on page 186. The lead contained in the filtrate may be determined by the method given on page 169.

WOOD'S METAL.

Alloy of Tin, Lead, Bismuth, and Cadmium.

The alloy is treated similarly to solder, the tin being separated and determined in the same manner. Since it is impossible to separate lead and bismuth by electrolysis, it is necessary to evaporate the solution to a sirup on the water-bath, add water and repeat the operation until the odor of nitric acid can be no longer detected. The solution is then treated with dilute ammonium nitrate solution, and the basic bismuth nitrate is filtered off.* A sufficient excess of nitric acid is added to the filtrate, and the lead is determined by electrolysis. The cadmium is precipitated by one of the methods given under Cadmium.

HARD LEAD. TYPE-METAL.

Alloy of Lead and Antimony (Copper).

The two metals may be separated, either by oxidizing with nitric acid, evaporating to dryness, and digesting the residue with sodium sulphide, or by heating the finely divided alloy with ten times its weight of anhydrous sodium thiosulphate in a covered porcelain crucible, over a very low flame, till the mixture is sintered together, and extracting with water. In either case, lead sulphide remains undissolved, and is filtered off, and washed first with sodium sulphide, and then with hydrogen sulphide, solution. It may be determined directly as sulphide, or as directed p. 169.

The antimony is determined, in the filtrate from lead sulphide, exactly as directed p. 180.

The following method is recommended by Neumann†: 2.5 g of the alloy are brought into a 250-cc graduated flask,

* Neumann, Analytischen Elektrolyse, Halle, 1897.

† Analytischen Elektrolyse, Halle, 1897.

10 g tartaric acid, 15 cc water, and 4 cc strong nitric acid are added, and solution is effected by warming. To the clear solution 4 cc of concentrated sulphuric acid is added, it is diluted somewhat, allowed to cool, and then diluted to the mark. 50 cc of the filtrate, corresponding to 0.5 g of the substance, is made strongly alkaline with sodium hydroxide, treated with 50 cc saturated sodium sulphide solution, heated to boiling, and immediately filtered. The filtrate, while still hot, is electrolyzed with a strong current according to the directions given on page 181. For the determination of the copper which is present, the residue remaining after treating with sodium sulphide is dissolved in nitric acid, the solution is diluted, and the copper separated as given on page 156. If the percentage of lead is also required, 0.5 g of the alloy may be taken and the precipitated lead sulphate determined gravimetrically; it is more satisfactory, however, to treat the solution of the metals directly with sodium hydroxide and sodium sulphide. The residue, consisting of the sulphides of lead and copper, is then dissolved in nitric acid, and the separation of the two metals is conducted under the conditions given on page 213.

ALLOY OF ANTIMONY AND TIN.

The method of analysis has been already given on p. 121. The alloy is oxidized with nitric acid, and the residue, after evaporation, dissolved in a concentrated solution of sodium sulphide, sodium hydroxide added, and the process followed throughout as given on p. 122.

ALLOY OF ANTIMONY AND ARSENIC.

It has already been stated (p. 224) that the two metals can be separated under conditions similar to those in the

separation of antimony from tin; the method requires the arsenic to be oxidized to arsenic acid. The alloy is digested with aqua regia, the acid removed by evaporation, the residue dissolved in concentrated sodium sulphide, sodium hydroxide added, and the directions given on p. 225 followed throughout.

ALLOY OF ANTIMONY, TIN, AND ARSENIC.

When this alloy is oxidized with aqua regia, and a solution in sodium sulphide prepared as above, antimony alone is electrolytically deposited in presence of tin. The method is described on p. 225.

SPATHIC IRON ORE.

Constituents: Ferrous Carbonate, with Manganese, Calcium, and Magnesium Carbonates (Gangue).

All the constituents of the mineral may be determined in the same solution. About 0.5 g of the dry mineral is dissolved in a porcelain dish, in the least possible amount of hydrochloric acid, the acid removed by evaporation, and the residue taken up with water to which a little hydrochloric acid is added. If insoluble gangue is present, this is filtered off, washed with water, and weighed. The metals are converted into oxalates by treatment with potassium and ammonium oxalate, and the insoluble residue of calcium oxalate filtered off, and washed with hot water. If manganese is present, the calcium oxalate always carries down some manganese oxalate.* When the precipitate is ignited, a mixture of CaO and Mn_2O_3 is obtained. It is weighed, and the manganese in it determined volumetrically.†

The iron and manganese are separated as directed on p. 195,

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* Classen, Zts. anal. Ch., 16, 318.

† Classen, Quant. Anal., 4th ed., p. 128.

the manganese finally precipitated as sulphide, and the magnesium in the filtrate as magnesium ammonium phosphate. If magnesium is absent, the manganese is determined as mangano-manganic oxide or sulphate (p. 196).

HEMATITE.

Constituents: Ferric Oxide, Manganic Oxide (Copper Oxide, Alumina, Lime, Magnesia), Phosphoric Acid, Sulphuric Acid.

The iron, manganese, and calcium are determined as above. If copper is present, it is first separated from the other metals by submitting the double oxalate solution to a very weak current. If, in addition to iron (copper, if present) and manganese, phosphoric and sulphuric acids are to be determined, the metals are converted into double oxalates, and iron and manganese completely removed (see separation of Iron and Manganese, p. 195); the two acids may now be determined in the solution entirely free from manganese. If only one acid is to be determined, the whole filtrate can be used; otherwise it is diluted to a known volume, and aliquot portions taken for analysis. In the determination of either acid, the solution is first acidified with hydrochloric acid,* and then treated either with barium chloride, or with one-third its volume of ammonia, and magnesium mixture. About 1 g of the mineral is needed for the determination of sulphuric and phosphoric acids.

If alumina, as well as phosphoric acid, is present in hematite (its presence is shown by a white turbidity† of

* If the acid carbonates produced from the oxalates are not decomposed, small hard crystals of acid carbonates are precipitated together with ammonium magnesium phosphate. These crystals are difficultly soluble in ammonia, and may make the results too high.

† A turbidity often appears when the solution is first heated, caused by the driving off of ammonium compounds.

aluminium phosphate and hydroxide in the solution undergoing electrolysis), the manganese must always be converted into sulphide. The iron-free solution is boiled to decompose hydrogen ammonium carbonate, tartaric acid or a solution of a tartrate added till the precipitate of aluminium hydroxide disappears, and the weakly ammoniacal solution precipitated hot with ammonium sulphide.

The green manganous sulphide is determined as heretofore directed. The phosphoric acid may be determined with magnesium mixture, in the filtrate from the manganese sulphide.

To determine sulphuric acid in presence of alumina, iron and manganese are removed, by electrolysis, from a separate portion, the solution is poured off, the ammonium carbonate decomposed by heat, the solution acidified with hydrochloric acid, and the sulphuric acid determined with barium chloride.

Determination of Iron, Manganese, Copper, Calcium, Magnesium, Phosphoric Acid, and Sulphuric Acid.

The method of determining iron, manganese, etc., in the same solution has already been given. If it is desired to determine magnesium and phosphoric and sulphuric acids, in the filtrate from manganese peroxide, it is diluted to a known volume, magnesium is determined in an aliquot part with ammonium phosphate, and phosphoric and sulphuric acids in two other portions.

LIMONITE.

Constituents: Ferric Hydroxide, together with Manganese Oxide (Lime, Magnesia), Phosphoric Acid, Sulphuric Acid, Silica, and Gangue.

The analysis may be conducted like those of hematite and spathic iron; but care must be taken, at the outset, to

convert the silica into the insoluble modification by evaporating the solution, and drying the residue.

CLAY IRON-ORE.

Constituents: Iron Oxide, Alumina, Manganese, and Water.

The mineral is digested with concentrated hydrochloric acid till it is completely decomposed, the insoluble residue is filtered off, the filtrate evaporated to remove free acid, the residue dissolved in water with a few drops of hydrochloric acid, and the iron separated from aluminium and manganese as directed pp. 194–198.

BOG IRON-ORE.

Mixture of Ferric Hydroxide with Ferrous and Ferric Silicates, Manganese, Alumina, Copper, Calcium, Magnesium, Sulphuric Acid, Phosphoric Acid, Arsenic Acid, Organic Matter, and Gangue.

The analysis of the mineral is easily understood from the foregoing.

Arsenic and copper are best determined by eliminating the former as chloride, as directed p. 226, and precipitating the copper with hydrogen sulphide in the greatly diluted residue left in the distillation flask. The copper sulphide is dissolved in nitric acid, and determined electrolytically as directed p. 156.

CHROME IRON ORE.

Constituents: Chromium Oxide, Ferrous and Ferric Oxides, Alumina, Manganese, Calcium, Silica.

The finely powdered mineral is fused for a long time with sodium carbonate and potassium chlorate, and the fused mass

extracted with water. The residue contains oxides of iron, manganese, calcium, magnesium, and aluminium, and traces of chromium and silica; the solution, chromic acid, silica, and some alumina and lime. The residue is dissolved in hydrochloric acid, the solution evaporated to dryness to separate silica, the residue treated with water and a little hydrochloric acid, and filtered. The metals in the filtrate are converted into double oxalates. If manganese is present, the precipitate of calcium oxalate must be treated as directed p. 239. The filtrate from the calcium oxalate, which contains iron, manganese, aluminium, and chromium, is treated as directed pp. 194–199. The aqueous solution from the fused mass is evaporated to separate silica, the calcium precipitated as oxalate, and the aluminium and chromic acid separated according to previous directions.

Edgar F. Smith recommends the use of the galvanic current for the decomposition of chrome iron ore. The process, according to his directions, is conducted as follows: Thirty or forty gm. potassium hydroxide are heated in a nickel crucible until the mass is in a condition of quiet fusion. The chrome iron ore for decomposition (about 0.5 gm.) is finely pulverized, weighed on a watch-glass, and gradually added, with the help of a camel's-hair pencil, to the crucible containing the fused alkali. The crucible is then covered with a perforated watch-glass and connected with the anode of the battery or other source of current. The kathode employed is a thick platinum wire, which is plunged through the opening in the watch-glass into the fused mass. To regulate the current an amperemeter (p. 31) is inserted, and a switch is also placed in the circuit, so adjusted as readily to produce the reversal of the current, which is necessary toward the close of the process. The current strength must not exceed 1 ampere. After about 30 minutes the current is reversed by the switch, so that the

crucible becomes the kathode, and the platinum wire the anode. The object of this reversal is to oxidize completely the last traces of the mineral, minute portions of which may have been protected by metallic iron which had been deposited by the current. After the current has acted in this direction for 10 minutes, the decomposition is complete. The fused mass of course contains the chromium as chromate.

The author pursued similar researches some years since, and can confirm Smith's results.

PSILOMELANE.

Constituents: Manganous Oxide, Copper Oxide, Ferric Oxide, Nickel Oxide, Cobalt Oxide, Alumina, Lime, Potash, Soda, and Lithia.

Determination of Manganese, Copper, Iron, Aluminium, Nickel, Cobalt, and Calcium.

A weighed portion of the mineral is dissolved in hydrochloric acid, evaporated to dryness, dissolved in water with a few drops of hydrochloric acid, converted into double oxalates, calcium oxalate filtered off, and the calcium and manganese in the precipitate determined as directed p. 239. In the filtrate, the copper is first determined electrolytically (p. 155). After the precipitation of the copper is complete, the solution, which contains the other metals, is decanted from the copper precipitate, and is then again submitted to electrolysis for the precipitation of iron, cobalt, nickel, and manganese, the latter as dioxide at the positive electrode. After the electrolysis is completed, the solution is decanted from the precipitated metals, and the remaining manganese completely precipitated, according to directions given on p. 196. If only the weight of nickel and cobalt together is desired, the precipitate containing the

three metals is dissolved in hydrochloric acid, and the iron determined by titration with potassium permanganate as directed p. 191. Otherwise the cobalt and nickel must first be separated from the iron. The precipitate of the metals is dissolved in hydrochloric acid, the acid removed by evaporation, the residue oxidized with hydrogen peroxide or bromine water, dissolved in water with a few drops of hydrochloric acid, and the metals converted into double oxalates by addition of potassium oxalate in slight excess. From the boiling solution, which should have a volume of 80–100 cc, the cobalt and nickel are precipitated as oxalates by concentrated acetic acid. A great excess of acetic acid must be used, and the solution, after the filtrate has subsided, must be tested with the reagent for a further precipitate. The filtrate from the cobalt and nickel oxalates contains all the iron as potassium iron oxalate.*

The precipitate of nickel and cobalt oxalates is washed with a mixture of equal parts of alcohol, acetic acid, and water, and, after drying to remove acetic acid and alcohol, is dissolved on the filter with hot water containing potassium and ammonium oxalates. The solution is electrolyzed as directed p. 141. The sum of nickel and cobalt is determined, the metals dissolved in hydrochloric acid, evaporated to dryness, the residue dissolved in a few drops of water, potassium hydroxide added in slight excess, and the resulting precipitate dissolved in concentrated acetic acid. The cobalt is precipitated with a saturated solution of potassium nitrite acidified with acetic acid. The precipitate, after standing twenty-four hours, is filtered off, washed with potassium nitrite, and dissolved in hydrochloric acid, the solution is

* Classen, Zts. anal. Ch., 18, 189

evaporated to dryness, and the residue converted into the double oxalate, and electrolyzed. The nickel is determined by difference. The nickel may also be determined, instead of, or in addition to, the cobalt, by precipitating nickel with potassium hydroxide, in the filtrate from the cobalt potassium nitrite, filtering, dissolving in hydrochloric acid, and separating nickel electrolytically as directed p. 144.

To determine the iron in the filtrate from cobalt and nickel oxalates, the alcohol and acetic acid are completely removed by evaporation, the residue dissolved in water, and the iron electrolytically deposited from the solution of the double oxalate (p. 138).

Determination of Potassium, Sodium, Lithium, Calcium, and Magnesium.

The mineral is dissolved in hydrochloric acid, evaporated to remove acid, and treated with an excess of ammonium oxalate. The filtrate from calcium oxalate is electrolyzed, iron, nickel, cobalt, and copper separating as metals, manganese as dioxide, and aluminium as hydroxide. The filtrate from the manganese dioxide and aluminium hydroxide contains only alkalies, magnesium, and a little manganese. It is boiled to remove the hydrogen ammonium carbonate formed by the electrolytic decomposition of ammonium oxalate, concentrated to about 50 cc, heated to boiling, and at least an equal volume of concentrated acetic acid added. The precipitate consists of manganese and magnesium oxalates. It is filtered off, washed with a mixture of equal volumes of alcohol, acetic acid, and water, and ignited. The residue is $MgO + Mn_2O_3$. It is weighed, dissolved in hydrochloric acid, and the manganese determined by electrolysis as dioxide (p. 150).

The alkalies are determined in the filtrate from the manganese and magnesium oxalates. It is evaporated to dryness, the ammonium salts removed by gentle ignition, the residue dissolved in water, the solution filtered, and evaporated to dryness after addition of a little hydrochloric acid. The residue is washed into a small stoppered flask with absolute alcohol, an equal volume of water-free ether added, and allowed to stand twenty-four hours. The solution is then filtered from the residue, the alcohol and ether evaporated, and the lithium chloride converted into sulphate and weighed.

The residue of potassium and sodium chlorides is dissolved in water, and both metals directly determined as directed p. 229.

SPHALERITE (ZINC BLENDE).

Constituents: Zinc Sulphide, also Determinable Quantities of Iron, Manganese, Copper, Arsenic, Antimony, and Gangue.

In most cases, it is only necessary to determine the zinc. The process is then as follows: About 0.5 g of the finely powdered mineral is digested with concentrated nitric acid till fully decomposed, the acid evaporated off, and the nitrates converted into chlorides by evaporation with hydrochloric acid. The residue is dissolved in about 25 cc water and 10 cc hydrochloric acid, and hydrogen sulphide passed through the solution. The precipitate of sulphides of lead, copper, etc., is filtered off, washed with water containing hydrogen sulphide and hydrochloric acid, and the filtrate evaporated to dryness. The residue contains chlorides of zinc, iron, manganese, calcium, and magnesium. It is dissolved in water with a little hydrochloric acid, converted into double oxalates (p. 138), the calcium oxalate filtered off, and the filtrate electrolyzed. Zinc and iron separate at the

negative electrode, and manganese, as dioxide, at the positive. The two metals are weighed, dissolved in hydrochloric acid, and the iron determined by titration with potassium permanganate (p. 191).

It is stated on p. 194 that the precipitation of iron and zinc from the same solution is complete only when there is less than one-third as much zinc as iron, and that it can be successfully performed, in other cases, by adding a weighed quantity of an iron salt before the electrolysis.

Determination of Lead, Copper, Arsenic, Antimony, Zinc, Iron, Manganese, and Gangue.

As when zinc alone is to be determined, the mineral is oxidized with nitric acid, the gangue filtered off, and the acid solution of chlorides treated with hydrogen sulphide. The precipitated sulphides are washed first with hydrogen sulphide water containing hydrochloric acid, and afterward with pure hydrogen sulphide water.

The antimony and arsenic are separated from lead and copper by digestion with a concentrated solution of sodium sulphide; the residue is washed with the same solution, and afterward with hydrogen sulphide solution. The sodium sulphide washings are added to the solution for determination of arsenic and antimony, and the hydrogen sulphide washings separately collected.

The necessary amount of sodium hydroxide is added to the sodium sulphide solution, and the antimony and arsenic separated and determined as directed p. 224.

The sulphides of lead and copper are dissolved in nitric acid, and the metals determined as directed p. 213.

Iron, zinc, and manganese are determined according to previous directions.

CALAMINE AND SMITHSONITE.

Constituents: Zinc (Cadmium), Copper, Lead, Arsenic, Antimony, Iron, Manganese, Calcium, Magnesium, Silica, Carbonic Acid, Water.

Zinc and the other constituents are determined as already directed. If the mineral contains cadmium, copper and lead are first precipitated from the nitric acid solution, the decanted solution evaporated to dryness, the cadmium nitrate converted into chloride, and cadmium determined as directed p. 163.

ULTRAMARINE.

Constituents: Alumina, Potassium, Sodium, Iron, Calcium, Sulphur, Silica, Sulphuric Acid, Chlorine.

A weighed portion of the substance is dissolved in hydrochloric acid, evaporated to dryness to separate silica, the residue dissolved in water with a few drops of hydrochloric acid, filtered from the silica, the free acid neutralized with ammonia, and a great excess of ammonium oxalate added. The calcium oxalate is filtered off, iron and aluminium determined electrolytically, the solution filtered from the aluminium hydroxide, evaporated to dryness, the ammonium salts removed by gentle ignition, the residue dissolved in water, and the alkalies converted into chlorides by evaporation with hydrochloric acid. Potassium and sodium are determined as directed p. 229.

REFINERY SLAG.

Constituents: Ferrous and Ferric Oxides, Metallic Iron, Copper, Aluminium, Calcium, Magnesium, Silica, Sulphuric and Phosphoric Acids.

A portion of the substance (0.5–1 g) is dissolved in hydrochloric acid, evaporated to remove silica, the residue dissolved in hydrochloric acid, evaporated to remove free acid, and the metals converted, as usual, into double oxalates. Calcium oxalate is filtered off, and the manganese in the precipitate determined as directed p. 239. The copper is separated by the action of a weak galvanic current (p. 156), and the iron, manganese, and aluminium separated in the copper-free solution as directed pp. 194–198.

For the determination of magnesium and sulphuric and phosphoric acids, see Hematite, p. 240.

To determine the metallic iron, about 5 g of the finely powdered slag is placed in a small platinum or porcelain dish, and treated with an aqueous solution of copper sulphate. A quantity of metallic copper equivalent to the iron is precipitated ($CuSO_4 + Fe = FeSO_4 + Cu$). The decomposition is hastened by frequent stirring; the copper and undecomposed slag are finally filtered off, washed thoroughly, and digested in the water-bath for a long time with nitric acid. In the solution, after filtration, the copper is electrolytically determined, and the quantity of iron calculated from it.

COPPER AND LEAD SLAGS.

Constituents: Copper, Lead, Iron, Manganese, Barium, Calcium, Magnesium, Silica, Sulphuric Acid, Sulphur, and ordinarily small quantities of Arsenic, Antimony, Bismuth, Cobalt, Nickel, and Zinc.

The slag is decomposed by digestion with nitric acid, evaporated to dryness, the residue taken up with water and

a little hydrochloric acid, and the solution filtered from the residue of silica and barium sulphate, which are separated as usual. The calcium is separated by adding ammonium oxalate in great excess; the calcium and the manganese it may contain are determined as directed p. 239. Copper is then precipitated (p. 155), and afterward iron and manganese (p. 194), and magnesium and sulphuric acid are determined as directed p. 240.

In the presence of arsenic, antimony, etc., the hydrochloric acid solution, after separation of silica, is treated, first hot and then cold, with hydrogen sulphide gas, and the precipitated sulphides are washed with hydrogen sulphide water, and treated with a concentrated solution of sodium sulphide. The insoluble sulphides of lead, copper, etc., are washed first with sodium sulphide, and then with hydrogen sulphide (see p. 237), and antimony and arsenic are separated in the solution as directed on p. 224.

The residue of lead sulphide, etc., is digested with nitric acid till thoroughly decomposed, and lead and copper separated from the solution as directed p. 213. The nitric acid is evaporated off, and bismuth determined as directed p. 237.

The solution filtered from the hydrogen sulphide precipitate, which contains iron, manganese, etc., is evaporated almost to dryness to remove hydrogen sulphide and most of the hydrochloric acid, and the metals finally converted into double oxalates. Calcium oxalate is filtered off, and the precautions described on p. 239 are observed in its determination. By electrolysis of the filtrate, iron, cobalt, nickel, and zinc are obtained as metals, and manganese, in part, as dioxide; magnesium remains in solution. The two latter are determined as directed p. 241.

The iron, cobalt, etc., are dissolved in concentrated hydrochloric acid, the solution evaporated to dryness, the residue

chloric acid, the solution evaporated to dryness, the residue dissolved in water with a few drops of acetic acid, potassium oxalate added in sufficient quantity to form the double oxalates, the solution diluted to 25–30 cc, and precipitated, at boiling heat, with concentrated acetic acid in great excess. After standing about six hours in a warm place, the oxalates of cobalt, nickel, and zinc are filtered off, washed with a mixture of equal volumes of acetic acid, alcohol, and water, and the oxalates converted, by very gentle heating, into oxides. The mixed oxides are dissolved in hydrochloric acid, and zinc separated from nickel and cobalt as directed on p. 234. Iron is determined, in the filtrate from the oxalates, as directed on p. 246.

BLAST FURNACE, CUPOLA, AND BESSEMER SLAGS.

Constituents: Ferrous and Ferric Oxides, Metallic Iron, Manganese, Aluminium, Copper, Lead, Zinc, Calcium, Magnesium, Alkalies, Silica, Sulphuric and Phosphoric Acids, Sulphur (as Calcium Sulphide).

The method of analysis is so similar to the foregoing that it needs only brief mention. The slag is digested with fuming hydrochloric acid, or aqua regia, till completely decomposed, the solution evaporated on the water-bath to dryness, the residue dissolved in water and a little hydrochloric acid, and the silica filtered off. After conversion into double oxalates, the calcium oxalate, which may contain manganese, is filtered off (p. 239), copper and lead first precipitated (p. 213), then iron and zinc with aluminium and the rest of the manganese; iron and zinc are determined as directed p. 193, and manganese, aluminium, and magnesium as directed p. 241. The alkalies and sulphuric and phosphoric acids are determined as heretofore directed.

ZIRCON.

Constituents: Zirconia, Iron Oxide, Lime, Silica.

The mineral is decomposed by long-continued fusion with sodium carbonate, the fused mass dissolved in hydrochloric acid, the solution evaporated to dryness, the residue taken up with water acidified with hydrochloric acid, the silica filtered off, and the filtrate treated with a great excess of ammonium oxalate. To overcome the injurious effect of sodium chloride, about 10 g ammonium oxalate must be dissolved by heating in the solution diluted to about 200 cc. The separation of iron and zirconium is carried out under conditions similar to those given for Iron-Beryllium, p. 201. If calcium is present, the calcium oxalate precipitate is, of course, to be filtered off before electrolysis, and determined.

ARSENOPYRITE.

Iron, Arsenic, Antimony, Sulphur, Gangue.

A portion of the finely powdered mineral is oxidized with aqua regia till fully decomposed, the gangue filtered off, and the solution evaporated to dryness. The chlorides are converted into sulphates by moistening and heating with sulphuric acid, water is added, the solution heated to 70°–80°, and hydrogen sulphide passed till it has cooled completely. After standing some twelve hours at a moderate heat, the sulphides of arsenic and antimony are filtered off, and separated as directed p. 224.

To determine the iron, the hydrogen sulphide is driven off from the solution, which is then treated as directed p. 138.

CHALCOPYRITE (COPPER PYRITES).

Constituents: Copper, Iron, Sulphur, Gangue.

The mineral is oxidized with nitric acid, the gangue filtered off, and copper precipitated in the filtrate (p. 156).

To determine iron, nitric acid is removed by evaporation, concentrated hydrochloric acid added, the solution again evaporated, and finally iron is precipitated, after formation of the double oxalate, according to directions on p. 138.

Sulphur may be determined in the same portion by precipitating sulphuric acid with barium chloride, and removing the excess of the latter by careful addition of sulphuric acid. Copper is then separated from iron in sulphuric acid solution, and the latter determined as usual.

As already stated on p. 157, copper cannot be precipitated from either nitric or sulphuric acid solution in the presence of any considerable quantity of arsenic and antimony without being contaminated by them.

If only the copper is to be determined, the nitric acid solution of the mineral is evaporated to dryness, the residue dissolved in water with a little acetic acid, and potassium oxalate added in excess. The solution is filtered hot from the gangue, the residue washed with water containing potassium oxalate, and the filtrate brought to a volume of about 50 cc. After cooling, almost all the copper crystallizes out as potassium copper oxalate; the rest is precipitated by addition of much concentrated acetic acid. The precipitate is washed with a mixture of equal volumes of water, acetic acid, and alcohol, dissolved in ammonium oxalate, and electrolyzed.

If arsenic and antimony are present in larger proportion, the finely pulverized mineral is mixed with four times its

weight of ammonium chloride, and heated gently in a covered crucible. Arsenic and antimony, and the greater part of the iron are volatilized as chlorides.*

The residue is dissolved in nitric acid, and treated as before.

NICKEL MATTE. COPPER MATTE.

Nickel, Cobalt, Zinc, Iron, Copper, Lead, Arsenic, Antimony, Sulphur, Gangue.

The substance is decomposed with aqua regia, evaporated to dryness, the residue dissolved in hydrochloric acid, and filtered from the gangue. In this solution, the metals precipitable by hydrogen sulphide are precipitated by heating to 70°–80°, and passing hydrogen sulphide gas till the solution becomes cold. The precipitate is filtered off, washed first with a solution containing hydrogen sulphide and hydrochloric acid, then with pure hydrogen sulphide solution, and treated with a concentrated solution of sodium sulphide as directed p. 222, and the arsenic and antimony separated and determined as directed p. 224.

The sulphides of lead and copper left undissolved by sodium sulphide are digested with nitric acid, and determined as directed p. 213. The filtrate from the hydrogen sulphide precipitate is evaporated to dryness to remove hydrogen sulphide and hydrochloric acid, the residue dissolved in water with a little acetic acid, potassium oxalate added in excess, and the solution of 50–100 cc precipitated boiling hot with a great excess of concentrated acetic acid (at least an equal volume). The precipitate of nickel, cobalt, and zinc oxalates is filtered off, washed with a mixture of equal volumes of alcohol, acetic acid, and water (p. 244),

* Classen, Zts. anal. Ch., 18, 388.

dried, and converted, by gentle ignition, into the oxides. The residue is dissolved in hydrochloric acid, and zinc, cobalt, and nickel separated, and determined as directed pp. 204 and 245.

Iron is determined, in the filtrate from the mixed oxalates, as directed p. 245.

COPPER SPEISS, LEAD SPEISS.

Antimony or Arsenic Compounds of Iron, Cobalt, and Nickel, together with Sulphur Compounds of Copper, Lead, Silver, Bismuth, Iron, and Zinc.

It is best to decompose the finely powdered substance in a suitable apparatus * with chlorine gas, volatilizing arsenic, antimony, iron, and zinc, as chlorides, and collecting them in a receiver containing equal volumes of hydrochloric and tartaric acids. The free chlorine is expelled, by heat, from the solution in the receiver, and hydrogen sulphide passed into the still hot solution until it cools. The sulphides are filtered, washed, treated with sodium sulphide, and arsenic and antimony determined in the solution, as directed p. 224. The insoluble sulphides of iron and zinc are dissolved in hydrochloric acid, evaporated to dryness, the residue dissolved in water with a few drops of hydrochloric acid, and iron and zinc determined as directed p. 193.

After the decomposition with chlorine, the non-volatile chlorides of copper, lead, silver, bismuth, cobalt, and nickel, and a part of the iron and zinc, remain in the bulb. They are dissolved in dilute hydrochloric acid, and lead, copper, silver, and bismuth precipitated with hydrogen sulphide. The sulphides are digested with nitric acid till completely

* Classen, Quantitative Analyse, 4th ed. p. 187.

dissolved, and copper and silver precipitated as metals, and lead as peroxide, by electrolysis. Copper and silver are separated as directed p. 216, and bismuth from some residual lead as directed p. 237.

The separation of cobalt and nickel from iron and zinc is given on pp. 204 and 244.

PYRARGYRITE.

Silver, Antimony (Arsenic), Sulphur, Gangue.

The mineral may be decomposed by chlorine gas, or by heating with anhydrous sodium thiosulphate. In the former case, the chlorides of antimony and arsenic (and sulphur) go into solution, while silver chloride remains in the bulb tube. In the latter case, when the fused mass is treated with water, silver sulphide remains undissolved, and may be dissolved in nitric acid, and the silver deposited, as metal, from the solution (p. 174).

To determine antimony, and separate it from arsenic, the solution of sodium pentasulphide is oxidized with hydrogen peroxide, evaporated, and treated as in the determination of antimony in presence of tin (p. 225).

TETRAHEDRITE.

Copper, Antimony, Arsenic, Silver, Lead, Iron, Zinc, Sulphur, Gangue.

The mineral may be decomposed as heretofore described. When chlorine gas is used, the receiver contains chlorides of antimony, arsenic, iron, and zinc (and sulphur); the bulb-tube, copper, lead, silver, and gangue, with a portion of the iron and zinc. The metals are separated as already described.

FURNACE "SOWS."

Alloys of Iron (the principal constituent), Copper, Silver, Lead, Molybdenum, Vanadium, Cobalt, Nickel, and Zinc, with Sulphides and Phosphides of these Metals, and varying amounts of Carbonic Acid and Silica.

The substance is best decomposed by chlorine gas. The quantity of iron is so great, however, that two bulb-tubes of the most infusible glass should be used, in the second of which is deposited most of the iron chloride. The substance is heated in a stream of chlorine as long as iron chloride sublimes; then it is certain that all the molybdenum chloride will have been carried over into the receiver, which also contains vanadium, sulphur, and phosphorus chlorides. Hydrogen sulphide is passed into the solution collected in the receiver until the supernatant liquid is colorless. The precipitate of molybdenum sulphide is filtered off, washed, oxidized with nitric acid, the solution supersaturated with ammonia, and molybdenum oxide precipitated by electrolysis.

The filtrate from molybdenum sulphide contains vanadium and iron. Hydrogen sulphide and hydrochloric acid are evaporated off, double oxalates formed, and the two metals separated electrolytically, according to the method given for the separation of Beryllium-Iron, p. 201. To determine vanadium in the solution decanted from the iron, it is evaporated to dryness, the ammonium salts driven off by careful ignition, and the residue of vanadium oxide converted, by fusion with potassium nitrate, into potassium vanadate. The fused mass is dissolved in water, nitric acid added not to acid reaction, then a concentrated solution of ammonium chloride, and then alcohol in the proportion of one volume to three of the solution. After standing forty-eight hours, the ammonium vanadate is filtered off, and washed with a concentrated solution of ammonium chloride,

and then with alcohol. The salt is heated first in the air, then in a stream of oxygen, and leaves a residue of pure vanadic acid which is weighed.

The chlorides remaining in the bulb-tube are heated with hydrochloric acid; a residue of silver chloride and carbon remains. It is heated with potassium cyanide, the carbon filtered off, and the silver determined by electrolysis.

The methods of separation and determination of the metals in the hydrochloric acid solution have already been given.

STIBNITE (ANTIMONY GLANCE).

Constituents: Antimony and Sulphur, and usually small quantities of Iron, Lead, Copper, and Arsenic.

The simplest method of analyzing the mineral is to mix with four or five times its weight of anhydrous sodium thiosulphate, and heat for a long time in a covered crucible (p. 237). The fused mass is extracted with water; the solution contains antimony and arsenic, and is treated for decomposition of sodium pentasulphide and determination of the two metals as directed p. 224; the undissolved sulphides of lead, copper, and iron are oxidized with nitric acid, and the metals separated according to foregoing directions.

ULLMANITE.

Antimony, Nickel, and Sulphur.

The finely powdered mineral is decomposed in a stream of chlorine (p. 256), all the antimony passing into the receiver as chloride, and nickel chloride remaining in the bulb-tube. The latter is determined by dissolving the contents of the bulb in hydrochloric acid, evaporating, converting into the double oxalate, and precipitating by electrolysis.

Antimony is precipitated, as sulphide, by passing hydrogen sulphide gas into the solution, in hydrochloric and tartaric acids, dissolved in concentrated sodium sulphide, the solution diluted with water and submitted to electrolysis (p. 179). If the mineral contains iron, it passes over, as chloride, into the receiver; it may be determined, in the filtrate from antimony sulphide, after supersaturation with ammonia, by precipitation as sulphide with ammonium sulphide. The sulphide thus obtained is dissolved, converted into the double oxalate, and iron determined electrolytically (p. 138).

The analysis is made more simply if the mineral is decomposed by heating with sodium thiosulphate; when the proportion of antimony is large, it is necessary to repeat the process with the residual nickel sulphide. Antimony is determined in the aqueous solution of the fused mass as directed p. 181. If, on treatment with hydrogen peroxide, or addition of sodium monosulphide, some nickel sulphide separates, it is added to the principal portion.

The sulphides of iron and nickel are oxidized with nitric acid, the nitrates converted into chlorides, and the two metals separated as directed (p. 192).

BOURNONITE.

Antimony, Lead, Copper (Iron), and Sulphur.

The finely powdered mineral is heated either with chlorine or anhydrous sodium thiosulphate, and the analysis conducted as already described.

ZINKENITE.

Antimony, Lead (Silver, Copper, Iron), Sulphur.

The mineral is most simply decomposed by heating with anhydrous sodium thiosulphate. After extracting with

water, the residue of undissolved sulphides is dried, the filter burnt, and fusion with thiosulphate repeated. Antimony is determined according to directions on p. 179. The sulphides of lead, silver, etc., are oxidized with nitric acid; copper and silver precipitated electrolytically, and separated as directed p. 216. A portion of the lead is separated, as peroxide, by the electrolysis of the nitric acid solution, and is determined as such. The rest is precipitated with hydrogen sulphide, the filtrate neutralized with ammonia, ammonium oxalate added, and iron determined by electrolysis.

LINNÆITE.

Constituents: Cobalt and Sulphur.

The analysis of this mineral is very simple. It is dissolved in aqua regia, the free acid evaporated off, and chlorides formed by repeated evaporation with hydrochloric acid.

The aqueous solution of the residue is treated with an excess of ammonium oxalate, and cobalt precipitated electrolytically (p. 141). If iron is present, the two metals are separated as directed p. 191.

In the solution decanted from the metallic cobalt, ammonium carbonate is decomposed by boiling, hydrochloric acid is added, and the sulphur determined by precipitation with barium chloride.

COBALTITE.

Cobalt, Iron (Copper, Antimony), Arsenic, and Sulphur.

The mineral may be decomposed by heating with nitric acid, or with sodium thiosulphate. If nitric acid is used, the free acid is evaporated off, and the nitrates converted

into chlorides. In the hydrochloric acid solution, arsenic, antimony, and copper are precipitated, as sulphides, by passing hydrogen sulphide into the hot solution till it cools; the sulphides are digested with sodium sulphide, and the solution treated as directed p. 224. The residue of copper sulphide is dissolved in nitric acid, and the copper separated by electrolysis (p. 156). The filtrate from the hydrogen sulphide precipitate is freed from hydrogen sulphide and hydrochloric acid, and iron and cobalt are separated as directed p. 191.

If the mineral is heated with anhydrous sodium thiosulphate, and extracted with water, antimony and arsenic go into solution, and are determined as directed p. 224.

The sulphides insoluble in water are dissolved in nitric acid, and copper first precipitated (p. 156); the nitrates are then converted into chlorides, and cobalt and iron determined (p. 191).

Finally, arsenic and antimony may also be determined by removing the arsenic first. The nitric acid solution is heated with sulphuric acid to convert nitrates into sulphates. The arsenic is driven off from this, as chloride, by treatment with ferrous chloride or sulphate, and distillation in a stream of hydrochloric acid (p. 226). To determine antimony, the residue in the flask is saturated with hydrogen sulphide, and filtered; the precipitate is washed, and treated with sodium sulphide (p. 227).

COBALTIFEROUS ARSENOPYRITE.

Cobalt, Iron, Arsenic, and Sulphur.

The mineral is analyzed in the same manner as cobaltite.

CERUSSITE.

Lead, Iron, Calcium, Carbonic Acid.

The pulverized mineral is dissolved by heating with nitric acid, and the lead determined, as peroxide, by connecting the platinum dish with the positive pole of the battery (p. 169).

The solution decanted from the lead peroxide is evaporated to dryness with hydrochloric acid, the residue taken up with water and a few drops of hydrochloric acid, treated with ammonium oxalate in great excess, calcium oxalate filtered off, and iron determined electrolytically in the filtrate (p. 138).

GALENA.

Lead (Antimony, Arsenic, Copper, Silver, Gold, Zinc, Iron), Sulphur, Gangue.

Galena rich in antimony is decomposed either by chlorine, or by heating with anhydrous sodium thiosulphate. When decomposed with chlorine, the receiver contains antimony, arsenic, iron, and zinc. These metals are separated as directed p. 256. The chlorides remaining in the bulb-tube are dissolved in hot dilute hydrochloric acid, and evaporated on the water-bath, with addition of sulphuric acid, till the hydrochloric acid is all driven off. The residue is diluted with water, one-third its volume of alcohol added to the solution, and the lead sulphate filtered off. In the filtrate, copper and silver are precipitated with hydrogen sulphide, the sulphides oxidized with nitric acid, and determined as directed p. 216.* The filtrate from the hydrogen sulphide

* As silver and gold are present only in small quantities, they are ordinarily determined by cupellation.

precipitate is evaporated, and iron and zinc determined as directed p. 193.

By heating galena with sodium thiosulphate, and extracting with water, antimony and arsenic (and gold) are found in the solution, and are separated as already directed; the sulphides of lead, silver, copper, zinc, and iron remain undissolved. The proportion of lead is so great that it cannot well be determined, as dioxide, in nitric acid solution; it is converted into sulphate, and the analysis completed as before.

PYROMORPHITE.

Lead Phosphate and Chloride, sometimes Sulphate and Arsenate.

The finely pulverized mineral is digested with nitric acid, and evaporated to dryness with hydrochloric acid. The residue is moistened with hydrochloric acid, dissolved in hot water, the clear filtrate poured off, and the lead chloride, which had crystallized out, brought into solution by repeated boiling with water. Lead and arsenic are precipitated by passing hydrogen sulphide into the hot solution till it cools, filtered hot after long standing, and the precipitate washed and digested with sodium sulphide. Arsenic is determined in the solution as directed p. 223. The lead sulphide is oxidized with nitric acid, and lead determined, as peroxide, as directed p. 168. Phosphoric acid is determined, in the usual way, in the filtrate from the hydrogen sulphide precipitate.

LEAD MATTE.

Lead, Copper, Iron (Silver, Antimony, Nickel, Zinc), Sulphur.

If the mineral is decomposed by heating in chlorine, iron and antimony pass over into the receiver. The analysis is conducted according to directions for copper or lead speiss.

CINNABAR.

Constituents: Mercury, Manganese, Copper, Alumina, Iron, Calcium, Sulphur.

The mineral is decomposed by heating with aqua regia, the solution evaporated on the water-bath, and the metals converted into nitrates by repeated evaporation with nitric acid. Mercury and copper are precipitated from the nitric acid solution (p. 175), the two metals redissolved in nitric acid, converted into the double cyanides, and determined according to the directions on p. 216. The small amount of manganese present is precipitated, as dioxide, in the electrolytic process, and may be weighed as such.

To determine iron, aluminium, and calcium, the solution decanted from the metals is evaporated to dryness on the water-bath, the nitric acid removed by repeated evaporation with hydrochloric acid, the weak acid solution of the residue treated with ammonium oxalate in great excess, calcium oxalate filtered off, and iron and aluminium determined as directed p. 197.

SOFT LEAD (CRUDE LEAD).

In addition to Lead, small quantities of Silver, Copper, Bismuth, Antimony, Arsenic, Cadmium, Iron, Zinc, Cobalt, Nickel.

According to the purity of the metal, 200 to 500 grams are taken. The weighed quantity, cleaned and rolled into thin plates, is digested with a mixture of about 250 cc concentrated nitric acid, sp. gr. 1.4, and 500–600 cc water. The solution is hastened by careful heating on a sand or water bath. If the acid works very actively, the flask is removed from the bath, but not long enough for crystals of lead

nitrate to separate from the cooled solution. If there is not more than 0.02–0.03 per cent of antimony, a perfectly clear solution is finally obtained. If the filtrate is turbid from the presence of lead antimonate, the precipitate is filtered off, and washed thoroughly with water (residue I).

The nitric acid solution is transferred into a 2-liter measuring-flask, about 170 cc of dilute sulphuric acid are added (1 part concentrated sulphuric acid and 2 parts water), thus precipitating all the lead as sulphate, and the flask is filled to the mark. The contents of the flask are thoroughly shaken, the precipitate allowed to settle, and the greater part of the solution siphoned off, taking care not to disturb the lead sulphate.

1,750 cc of the clear solution are evaporated till white fumes of sulphuric acid appear; 50–60 cc of water are added after cooling, and the small amount of lead sulphate that may remain undissolved is filtered off. As this latter may contain antimony, it is digested with concentrated sodium sulphide, and the solution siphoned off (solution I).

The filtrate from lead sulphate is heated to about 70°, and hydrogen sulphide passed in till it cools. When the precipitate, after long standing on the sand-bath, has completely subsided, it is filtered off, washed thoroughly with water containing hydrogen sulphide, and digested with a concentrated solution of sodium sulphide. The residue marked I is also treated with sodium sulphide, and the dissolved portion, together with solution I, added to the principal solution. Antimony and arsenic are then separated and determined as directed p. 224.

The sulphides insoluble in sodium sulphide (copper, cadmium, etc.) are digested with nitric acid till completely oxidized, and copper and silver are separated from the solution, as metals, by electrolysis, and any remaining lead

as peroxide. The copper and silver are separated and determined as directed p. 216.

To determine bismuth and cadmium, the nitric acid is completely removed by evaporation, the residue dissolved in water with a few drops of dilute hydrochloric acid, potassium cyanide added, and the solution gently heated on the water-bath; the potassium bismuth cyanide is filtered off and washed with water. The bismuth may then be determined gravimetrically.

Cadmium can be directly electrolyzed from the solution of cadmium potassium cyanide (p. 165).

The filtrate from the original hydrogen sulphide precipitate, which contains zinc, iron, cobalt, nickel, etc., is heated to boiling and oxidized with bromine-water. An excess of sodium hydroxide is added, and the metals, with the exception of zinc, are precipitated as hydroxides. The solution is filtered off, and the zinc precipitated by electrolysis, either directly from the filtrate, or after being first converted into some other salt. The hydroxides are dissolved in dilute sulphuric acid, the iron is precipitated with ammonium hydroxide and determined either gravimetrically or by electrolysis. The nickel and cobalt are determined in the solution, from which the iron has been removed, by electrolysis under the conditions given on p. 144.

In calculating the analysis, the space occupied by the lead sulphate in the solution is to be taken into account. 100 g lead converted into sulphate occupy a space of 23 cc; 200 g, therefore, 46 cc. Accordingly in making the calculation, 1750 cc are to be reduced, not to 2000 cc, but to $2000 - 46 = 1954$ cc, or to 179.12 g lead.

Crude lead is also analyzed by the foregoing method; 10 to 50 g is a sufficient quantity for the analysis.

ANTIMONY.

Metallic antimony may be treated in the same way as hard lead, p. 237.

SPELTER (CRUDE ZINC).

Zinc and determinable quantities of Lead, Iron, Cadmium, Arsenic, Antimony, Tin, and Copper.

In the analysis of crude metals, the determination of the impurities is of more importance than that of the metal. As the quantity of other metals is so small, it is necessary to dissolve a large quantity of zinc. According to its purity, 25 to 100 g are taken, and dissolved, in a flask, by gradual addition of hydrochloric acid, some zinc, however, being left undissolved. If the zinc comes in sticks, a stick may be fastened to a platinum wire, and dipped partly into the solution, and the undissolved zinc removed, cleaned, and weighed.

In both cases, zinc only goes into solution; the other metals, with the exception of arsenic and antimony, being left as spongy masses. It is necessary, however, to filter the solution of zinc at once, and to wash the residue. The latter is digested with nitric acid, and carbon and silica, with all the tin oxide and small quantities of antimony (most of it was volatilized during the solution in hydrochloric acid) and lead, remain undissolved. To determine the tin, the residue is heated with concentrated hydrochloric acid, carbon and silica are filtered off, the filtrate is evaporated to dryness, and the residue digested with a concentrated solution of sodium sulphide. The antimony and tin in the filtered solution are separated as directed p. 221.

The nitric acid solution of the metals is evaporated, the

residue dissolved in dilute hydrochloric acid, diluted with water, and hydrogen sulphide passed into the hot solution till it has thoroughly cooled. The precipitate, after settling, is filtered off, washed with water, and digested with concentrated sodium sulphide. The sulphides of lead, copper, etc., remain, are dissolved in nitric acid, and separated as in the analysis of soft lead.

The filtrate from the hydrogen sulphide precipitate is heated to boiling and treated with bromine-water; and the metals present, iron, zinc, nickel, cobalt, etc., determined as in the analysis of soft lead.

Antimony and arsenic must be determined in a separate portion of zinc, which is dissolved in aqua regia. The aqua regia is evaporated off, the residue treated with concentrated hydrochloric acid, and again evaporated, and finally dissolved in dilute hydrochloric acid. Hydrogen sulphide is passed into the solution as before, the sulphides are filtered off after long standing, washed thoroughly with water, and digested with a concentrated solution of sodium sulphide. Antimony and arsenic and tin, if present, are determined as directed pp. 225 ff.

BLISTER COPPER.*

Copper, Iron, Lead, Silver, Antimony, Arsenic, Bismuth, Zinc, Nickel, Cobalt.

Fifty grams of blister copper must be taken to determine the impurities; it is analyzed in two separate portions of

* Process of analysis partly after W. Hampe ("Beiträge zur Metallurgie des Kupfers"), Zts. für Berg-, Hütten- und Salinenwesen, **27**, 205.

25 g each. Each portion of 25 g of bright copper cuttings is digested with a mixture of about 175 cc nitric acid, sp. gr. 1.2, and 200 cc water, till no metallic residue is left; and after cooling, whether the solution is clear or not, 25 cc of concentrated sulphuric acid are carefully added. The solution is evaporated on the water-bath, and heated on the sand-bath till the excess of sulphuric acid is driven off. After cooling, 20 cc nitric acid is added, the solution is diluted with 300 or 400 cc water, and heated to dissolve copper sulphate.

This solution is treated with *exactly* enough* of a titrated solution of hydrochloric acid to precipitate the silver, and allowed to stand twenty-four hours, after which the precipitate (I.) of silver chloride, lead sulphate, antimony oxide, etc., is filtered off and washed with water.

The filtrate is brought to a volume of 400–450 cc, and the copper separated by electrolysis. For this purpose, either a larger platinum dish is used, or the platinum cone shown in Fig. 61, p. 88; and the current is continued only so long as is necessary to remove the copper, as otherwise it might be contaminated with antimony and arsenic. If the copper is darkened by these metals, the process given on p. 157 must be followed.

There is usually a slight deposit of lead peroxide on the positive electrode which is determined as directed p. 169. The precipitated copper contains bismuth. To determine the latter, the copper precipitated from both 25-g portions is dissolved in about 350 cc nitric acid, sp. gr. 1.2; a great excess of concentrated hydrochloric acid added, and the solution boiled till all the nitric acid is driven off. It is evaporated on the water-bath till the residue has a brown

* Silver must be previously determined in a separate portion of 25 g.

color, and then poured into a large quantity of boiling water to separate the bismuth as oxychloride. The bismuth oxychloride is generally contaminated with some basic copper salt. If the color shows the quantity of the latter to be considerable, the precipitate, after standing twenty-four hours, is filtered off, dissolved again in concentrated nitric acid, diluted with water, and copper precipitated electrolytically (p. 156).

The bismuth in the solution is determined gravimetrically.

The solution siphoned off from the main portion of the copper is evaporated to dryness, and the sulphuric acid set free by the precipitation of copper removed by heating on the sand-bath, so that the residue contains only traces of acid. After cooling, it is dissolved in hydrochloric acid and water, any silica from the glass vessels filtered off, and hydrogen sulphide passed into the solution, heated to 70°–80°, till it is thoroughly cool. The precipitate, which consists mostly of arsenic and antimony, is filtered off after long standing on the sand-bath, and washed; the filtrate, containing iron, cobalt, etc., is retained (II.).

Another portion of the antimony is in residue I., which was left on the solution of the blister copper in nitric acid. Both precipitates are digested with a concentrated solution of sodium sulphide, filtered, and antimony and tin determined as directed p. 222. The sulphides insoluble in sodium sulphide are oxidized with nitric acid, silver (p. 172), and lead (p. 169) precipitated from the solution, the solution siphoned off, evaporated to remove nitric acid, and bismuth determined gravimetrically.

Solution II. filtered from the hydrogen sulphide precipitate, which contains iron, cobalt, etc., is evaporated to remove hydrogen sulphide, etc., and the metals are determined in the residue as directed p. 267.

REFINED COPPER.

This contains, in addition to the metals present in blister copper, *cuprous oxide*. The metals are determined as in blister copper. The determination of the cuprous oxide is based on the fact that it reacts with a *dilute* neutral silver solution, with the formation of metallic silver and basic copper nitrate, which precipitate, and normal copper nitrate, which remains in solution.

$$3Cu_2O + 6AgNO_3 + 3H_2O = 2Cu_2(OH)_3NO_3 + 2Cu(NO_3)_2 + 6Ag.$$

The process is as follows: About 2 g silver nitrate is dissolved in 100 cc water, and about 1 g of the copper to be tested is added. When the reaction is ended in the cold, the precipitate is filtered off, and washed thoroughly with water; either the copper or the silver in it may be determined electrolytically. The nitric acid is removed by evaporation, and copper and silver separated as directed p. 216. If copper is to be determined, silver is precipitated as silver chloride from the aqueous solution of the residue, the excess of acid removed, and copper precipitated, by electrolysis, from solution of copper ammonium oxalate (p. 155).

TIN.

The Impurities are usually Copper, Lead, Bismuth, Iron, Zinc, Arsenic, and Antimony.

By oxidation of the metal with nitric acid, the tin is completely converted into insoluble oxide, while the other

metals remain, for the most part, in solution. The tin oxide contains, however, determinable quantities of lead, copper, antimony, and arsenic. The methods already described are used for their separation; the tin oxide is digested with a concentrated solution of sodium sulphide, or fused with anhydrous sodium thiosulphite in a porcelain crucible.

The insoluble sulphides of copper and lead are oxidized with nitric acid, and the solution added to the principal solution of the metals. The rest of the process is in accordance with previous directions.

SILVER.

Traces of Gold, also Lead, Copper, Antimony, and Arsenic.

The gold remains undissolved when a large quantity of silver is dissolved in nitric acid entirely free from hydrochloric acid. To determine copper and lead, the silver is precipitated from the largely diluted solution by hydrochloric acid, the silver chloride filtered off, and copper and lead separated, after removal of hydrochloric acid, as directed p. 213.

As antimony and arsenic can only be present in very small quantities, they are determined in a larger weight of silver. The silver is precipitated as chloride, and the metals precipitable by hydrogen sulphide by passing the gas into the hot filtrate. Antimony and arsenic are separated from the other metals by digestion with sodium sulphide, and determined as usual (p. 224).

COMMERCIAL NICKEL.

Nickel, Copper, Arsenic, Antimony, Iron, Cobalt (Carbon, Silica, Sulphur).

The nickel is dissolved in nitric acid, the insoluble residue filtered off, the nitric acid removed by evaporation, the residue dissolved in hydrochloric acid, and hydrogen sulphide passed in to remove the metals which it will precipitate. It is best to redissolve the sulphides and repeat the precipitation. Antimony and arsenic are separated from copper by digesting the sulphide with sodium sulphide, and determined as usual. It is to be noted, in determining antimony, that the insoluble residue (silica, etc.) may contain antimony, and must be tested for it.

To separate cobalt and nickel from iron, the filtrate from the hydrogen sulphide precipitate is evaporated to dryness, the residue oxidized with hydrogen peroxide or bromine water, and dissolved in water with addition of acetic acid. The metals are then converted into double oxalates by addition of potassium oxalate, and cobalt and nickel precipitated by acetic acid. The two metals, and the iron in the filtrate, are determined as directed p. 245.

If only iron is to be determined, the three metals are precipitated from the double oxalate solution by electrolysis, the weight ascertained, and the iron determined volumetrically in hydrochloric acid solution (pp. 191–193).

PIG IRON, STEEL, SPIEGEL, FERROMANGANESE.

Constituents: Iron, Manganese, Copper, Zinc, Cobalt, Nickel, Chromium, Aluminium, Titanium, Arsenic, Antimony, Calcium, Magnesium, Silicon, Phosphorus, Sulphur, Carbon.

If a complete analysis of iron is to be made, it is best to dissolve a large quantity, dilute to a known volume, and use aliquot parts of the solution. In many cases, only copper, or manganese, or certain other metals are to be determined. The complete analysis will first be described, and afterward the special determination of certain metals. 5 or 10 grams of the pure iron, in powder or turnings, are dissolved in hydrochloric acid in a capacious platinum or porcelain dish, and the solution evaporated to dryness. The residue is moistened with dilute hydrochloric acid, allowed to stand for a time that the acid may act, dissolved in water, and the insoluble residue of graphite, silica, and compounds of iron with titanium, chromium, phosphorus, and carbon, filtered off. The precipitate is ignited with the filter, fused with about its own weight of a mixture of equal parts of sodium carbonate and potassium nitrate, dissolved in water with addition of hydrochloric acid, and the solution evaporated on the water-bath. The residue is heated for a short time on the sand-bath to insure separation of silica, moistened, after cooling, with hydrochloric acid, treated with water, heated, and the silica filtered off, weighed, and tested for titanium. The filtrate contains chromium, together with the rest of the silica and titanium, and small quantities of iron and aluminium. To completely separate silica and titanium, the solution is evaporated to dryness, the residue treated with

dilute sulphuric acid, and heated till all the hydrochloric acid is driven off; water is then added, silica filtered off, and titanic acid precipitated by long boiling. The filtrate from titanic acid is concentrated by evaporation, the free sulphuric acid neutralized with ammonia, iron, aluminium, and chromium converted into the double oxalates, and chromium separated as directed p. 153.

For the determination of *iron*, *aluminium*, *zinc*, *cobalt*, *nickel*, *manganese*, *copper*, *calcium*, and *magnesium*, an aliquot part of the hydrochloric acid solution is saturated with hydrogen sulphide, and the precipitate filtered off after long standing in a warm place.

Since arsenic and antimony are ordinarily present only in very small quantities, the copper sulphide can usually be oxidized with nitric acid, and the copper determined electrolytically. If the precipitated copper is blackened by the presence of antimony or arsenic, it is treated as directed p. 157.

The filtrate from the hydrogen sulphide precipitate is freed from hydrogen sulphide and hydrochloric acid by evaporation, oxidized with hydrogen peroxide or a little bromine water (by no means with nitric acid), dissolved in water with addition of a little acetic acid, and the metals converted into double oxalates by the use of potassium (not ammonium) oxalate. The insoluble calcium oxalate is filtered off, and separated from the manganese precipitated with it as directed p. 239. The filtrate is diluted * with water, heated to boiling, and an excess of concentrated acetic acid added, whereby all the zinc, cobalt, nickel, and magnesium, and a portion of the manganese, are precipitated as oxalates; iron, aluminium, and the rest of the manganese remain in solution

* Fifty cc of the dilute solution should contain 0.4–0.5 g iron.

as double oxalates. The beaker is covered, and left standing in a warm place for six hours; the precipitate is then filtered off, washed with a mixture of equal volumes of acetic acid, water, and alcohol, and dissolved, after drying, in ammonium oxalate. Zinc, cobalt, and nickel are separated from manganese and magnesium as directed p. 251. The filtrate from the oxalates is completely freed from alcohol and acetic acid by evaporation, and iron, aluminium, and manganese separated as directed pp. 194–198. As the quantity of zinc, cobalt, etc., is generally very small, it is best, in order to facilitate the separation of the oxalates and the collection of the precipitate, to add about 0.2 g magnesium in the form of chloride,* so that magnesium oxalate is precipitated with the other oxalates. In this case, the magnesium in pig iron, if present at all, is determined in another portion, together with some other metal (e.g., copper). If magnesium is used, all the manganese is found in the precipitate produced by acetic acid.

To determine manganese alone in pig iron, either an aliquot part of the hydrochloric acid solution, or a separate portion of 0.2–0.5 g iron may be taken, and the determination conducted as directed under Spathic Iron Ore, p. 239. If copper is to be determined, the solution freed from acid and preferably oxidized is treated with ammonium oxalate in great excess, and electrolyzed as already directed. The hydrochloric acid solution may also be precipitated with hydrogen sulphide, and the copper determined in nitric acid solution (see p. 156).

Determination of Arsenic and Antimony.

Since these metals are present only in very small quantity, about 10 g pig iron are used for their determination, and

* Dissolve magnesium oxide in hydrochloric acid, and remove the free acid by evaporation.

digested with aqua regia. When solution is complete, the aqua regia is removed by evaporation, the residue treated with hydrochloric acid, and heated till no nitric acid remains.

The solution is diluted, heated, and hydrogen sulphide passed into it until it is thoroughly cool (p. 253); the precipitated sulphides of arsenic, antimony, and copper are filtered off, thoroughly washed, and digested with sodium sulphide. The solution is treated like one containing polysulphides, and arsenic and antimony separated as directed p. 224.

Determination of Phosphorus.

About 2 g of iron is digested with nitric acid, sp. gr. 1.2, till decomposition is complete. If a carbonaceous residue is left, the nitric acid solution is poured off, and the residue heated with aqua regia. Nitric acid and aqua regia are completely removed by evaporation to dryness, and the nitrates converted into chlorides by repeatedly moistening with concentrated hydrochloric acid, and evaporating to dryness. The residue is treated with water, heated, and the iron brought into solution by the addition of the least possible quantity of hydrochloric acid. To convert the iron, etc., into double oxalates, six or eight times the weight of the iron, reckoned as oxide, of a mixture of 1 part potassium oxalate and 5–6 parts ammonium oxalate, is dissolved by heating in the solution, it is diluted to 250–300 cc, and electrolyzed at a temperature of about 80°. The heating is maintained during the reaction; the solution must by no means be heated to boiling, lest the iron scale off. The solution is poured off when the reduction is complete, and phosphoric acid determined as magnesium pyrophosphate.

Two grams of iron are enough for the determination of

phosphorus, even when the percentage is small. If a larger quantity is taken, it is best to divide the solution, after conversion into oxalates, and precipitate in several dishes.

As it is not necessary to determine the iron, it may be precipitated just as well in a beaker; in this case, the negative electrode is a large piece of light platinum foil which is attached by a platinum wire to the negative pole of the source of current.

Determination of Sulphur.

About 2 grams of iron is oxidized, with aqua regia, to convert sulphur into sulphuric acid, and the insoluble residue filtered off. As a portion of the sulphur may be left in the residue, it is fused with a *small* quantity of a mixture of sodium carbonate and potassium nitrate, the fused mass dissolved in hydrochloric acid, and the solution thus obtained added to the other. The aqua regia is removed, the nitrates converted into chlorides, and the latter into double oxalates, as already directed. After removing the iron by electrolysis, the solution is poured off, boiled to remove ammonia, acidified with hydrochloric acid, and the sulphuric acid precipitated with barium chloride.

TABLES FOR CALCULATION OF ANALYSES.

	Atomic Weight.	Found.	Required.	Factor.
Aluminium . .	27.04	Al_2O_3	Al	0.5304
Antimony . .	119.6	Sb	Sb_2O_3	1.20017
			Sb_2S_3	1.40108
Arsenic . . .	74.9	As	As_2O_3	1.31962
			As_2O_5	1.53271
			As_2S_3	1.64192
Barium . . .	136.86	$BaSO_4$	Ba	0.58819
		$BaCO_3$	Ba	0.69574
			BaO	0.77688
Beryllium . .	9.08	BeO	Be	0.36262
Bismuth . . .	208.4	Bi	Bi_2O_3	1.11488
Boron	10.9	KBF_4	B	0.08639
			B_2O_3	0.27613
Bromine . . .	79.76	AgBr	Br	0.42556
Cadmium . . .	111.7	Cd	CdO	1.14288
			CdS	1.28630
Cæsium . . .	132.7			
Calcium . . .	39.91	CaO	Ca	0.71433
		$CaCO_3$	Ca	0.40006
			CaO	0.56004
Carbon . . .	11.97	CO_2	C	0.272727
		$CaCO_3$	CO_2	0.43995
Cerium . . .	141.2			
Chlorine . . .	35.37	AgCl	Cl	0.24729
		Ag	Cl	0.32853
Chromium . .	52.0	Cr_2O_3	Cr	0.81419
			CrO_3	1.18581

	Atomic Weight.	Found.	Required.	Factor
Cobalt . . .	58.60	Co	CoO	1.27116
Copper . . .	63.18	Cu	CuO	1.25261
			CuS	1.25309
Didymium . .	145.0			
Erbium . . .	166.0			
Fluorine . . .	19.06	CaF_2	F	0.48853
Gold	196.7	Au	Au_2O_3	1.12171
Hydrogen . .	1	H_2O	H	0.11136
Iodine. . . .	126.54	AgI	I	0.54031
		Ag	I	1.17546
Iron	55.88	Fe	FeO	1.28561
			Fe_2O_3	1.42812
Lanthanum . .	138.5			
Lead	206.39	PbO_2	Pb	0.86605
			PbO	0.93303
			$PbCl_2$	1.16289
Lithium . . .	7.01	LiCl	Li	0.165408
			Li_2O	0.35370
		Li_3PO_4	Li	0.18156
			Li_2O	0.38824
			LiCl	1.09764
Magnesium . .	23.94	$Mg_2P_2O_7$	Mg	0.21614
			MgO	0.36024
Manganese . .	54.8	Mn_3O_4	Mn	0.72029
			MnO	0.93007
			Mn_2O_3	1.03496
		MnO_2	Mn	0.63192
			MnO	0.81596
			Mn_2O_3	0.90798
		$MnSO_4$	Mn	0.36383
			MnO	0.46979
			Mn_2O_3	0.52277

	Atomic Weight.	Found.	Required.	Factor.
Mercury . . .	199.8	Hg	Hg_2O	1.03994
			HgO	1.07988
			HgCl	1.17703
			Hg_2S	1.08003
			HgS	1.16006
Molybdenum .	95.9	MoS_3	Mo	0.49989
Nickel	58.6	Ni	NiO	1.27116
Niobium . . .	93.7			
Nitrogen . . .	14.01	Pt	N	0.14411
			NH_3	0.17497
			NH_4	0.18526
Osmium . . .	195			
Palladium . .	106.2			
Phosphorus . .	30.96	$Mg_2P_2O_7$	P	0.27952
			P_2O_5	0.63976
Platinum . . .	194.43	Pt	PtO_2	1.16417
Potassium . .	39.03	Pt	K	0.40129
			K_2O	0.48848
			KCl	0.76495
			K_2SO_4	0.89389
Rhodium . . .	104.1			
Rubidium . .	85.2			
Ruthenium . .	103.5			
Selenium . . .	78.87			
Silicon . . .	28	SiO_2	Si	0.46729
Silver	107.66	Ag	Ag_2O	1.07412
			AgCl	1.32853
Sodium . . .	22.99	NaCl	Na	0.39393
			Na_2O	0.53067
			Na_2SO_4	1.21488
Strontium . .	87.3	$SrSO_4$	Sr	0.47673
			SrO	0.56389

	Atomic Weight.	Found.	Required.	Factor.
Sulphur . . .	31.98	$BaSO_4$	S	0.13744
			SO_3	0.34322
			SO_4	0.41181
Tantalum . .	182			
Tellurium . .	127.7			
Thallium . . .	203.7	Tl_2O	Tl	0.9623
Thorium . . .	231.96			
Tin	118.8	Sn	SnO_2	1.26869
Titanium . . .	50.25	TiO_2	Ti	0.61154
Tungsten . . .	183.6	WO_3	W	0.79316
Uranium . . .	239.8	UO_2	U	0.88249
			U_3O_8	1.03916
Vanadium . .	51.1	V_2O_5	V	0.56154
Yttrium . . .	89.6			
Zinc	65.1	Zn	ZnO	1.24516
			ZnS	1.49124
Zircon . . .	90.4	ZrO_2	Zr	0.73904

REAGENTS.

POTASSIUM OXALATE.

The crystallized potassium oxalate of commerce always contains determinable quantities of iron and lead. To purify it, one part of the salt is dissolved in three parts of water in a porcelain dish, and ammonium sulphide is added drop by drop, as long as a precipitate forms. The solution is now heated on the water-bath till the precipitate settles, and filtered through a plaited filter. To decompose the slight excess of ammonium sulphide, a current of air is conducted through the solution till it is perfectly colorless, and no longer gives a reaction with sodium nitroprusside. The separated sulphur is allowed to settle, and the clear solution siphoned off.

AMMONIUM OXALATE.

The same impurities are present as in potassium oxalate. The salt is purified by precipitating the hot saturated solution with ammonium sulphide. It is heated over a naked flame till the precipitate coheres together, and filtered hot by the use of a hot-water funnel. The greater part of the ammonium oxalate crystallizes from the filtrate on cooling. The solution is poured off, and the crystals dried by placing them in a funnel stopped with asbestos, and connecting with a filter-pump.

OXALIC ACID.

The impurities are similar to those of the alkali oxalates; it is purified by repeated recrystallization.

AMMONIUM SULPHATE.

This salt is purified in the same way as ammonium oxalate.

SODIUM SULPHIDE.

The crystallized sodium sulphide of commerce is not only exceedingly impure, but is not monosulphide at all, but a mixture of polysulphides and sodium hydroxide. The presence of the latter explains that of alumina, which is always found in abundance. If commercial sodium sulphide is used, its solution must first be *completely saturated*, without access of air, with hydrogen sulphide gas. It is better, however, to prepare the substance, in which case the process is as follows: Sodium hydroxide purified by alcohol is dissolved in water to a solution of sp. gr. 1.35. The solution is divided into two equal parts, and one half, with exclusion of air, saturated with the purest possible hydrogen sulphide gas till the volume ceases to increase. The hydrogen sulphide is purified by passing it through a wash-bottle of water, and several tubes filled with cotton or wadding. When completely saturated, the solution is filtered from the precipitate formed, and mixed with the other half of the sodium hydroxide solution. Hydrogen sulphide is again passed into the mixture, with exclusion of air, and it is filtered again. The nearly colorless filtrate is evaporated in a capacious platinum or porcelain dish, over a *strong* free flame as quickly as possible. It boils without bumping if a platinum spiral is

plaeed in it. As soon as a thin crystalline pellicle forms on the surfaee, the boiling is stopped, and the solution poured while hot into small flasks with well-ground glass stoppers which must be filled full. It is best to eompletely exclude the air by melted paraffine. For the separation of antimony and tin, the solution should have a sp. gr. of 1.22–1.225.

ALCOHOL.

The aleohol used for washing metals must be free from acid, and, as nearly as possible, absolute. It is left standing in a large flask, for twelve hours, over quicklime, and then distilled off on a water or steam bath. The distillate must leave no residue on evaporation.

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